

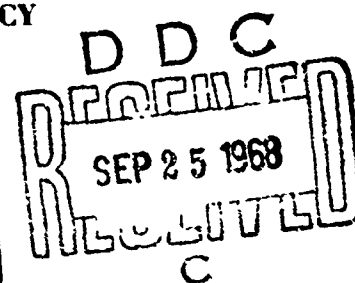
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ANNUAL REPORT 1967-1968

including results of research on
MATERIALS PREPARATION AND CHARACTERIZATION

supported by the
ADVANCED RESEARCH PROJECTS AGENCY
under

Contract DA-49-083 GSA-3140



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MATERIALS RESEARCH LABORATORY
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA

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Dedicated to our colleague
Professor Wilhelm R. T. Buessem
on the occasion of his retirement.

ANNUAL TECHNICAL PROGRESS REPORT

for the period

July 1, 1967 - June 30, 1968

incorporating work on

"MATERIALS PREPARATION AND CHARACTERIZATION"

supported by the

ADVANCED RESEARCH PROJECTS AGENCY

Contract DA-49-083, OSA 3140

August 15, 1968

**Materials Research Laboratory
The Pennsylvania State University**

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- 1.1 Nature of this Report. This document reports the overall research interests of the Materials Research Laboratory of The Pennsylvania State University and the individual activities of the faculty affiliated with it. The survey covers, but is not limited to, the research supported by the Advanced Research Projects Agency under Contract No. DA 49-083 OSA 3140, and serves as the Annual Report for this contract. Research in the area of materials science and engineering is conducted under several organizational units at Penn State, not all of which are connected with the Materials Research Laboratory, the University's interdisciplinary, intercollege organization in this field. The research of intra-college units working on materials does not appear in this report.

The subject matter grouping used below does not follow the traditional disciplinary and departmental subdivisions. Instead, as is appropriate for an interdisciplinary organization, the report brings together under new headings the inter-related work conducted by faculty members with backgrounds in a variety of disciplines:

Preparation of Materials, including synthesis, thermodynamics, equilibria, kinetics, and crystal growth of inorganic materials.

Characterization of Materials, which encompasses only those studies which provide, directly, information on the chemical composition or the atomic structure of the phases.

Properties of Materials, which includes the work on the elastic, magnetic, electrical and optical properties of solids.

The Glass Program, which represents a "horizontal cut" across the other groupings and is made because of the emphasis we have urged upon ARPA in this area, and the subsequent three-way cooperative program developed by the Naval Research Laboratory, Bausch and Lomb and Penn State.

2.0 OVER-VIEW OF LABORATORY ACTIVITY

The laboratory continued to grow although at a reduced rate during the last year in spite of the unfavorable financial climate. The growth is reflected in the scope of the activities, the number of Ph. D. and M. S. degrees granted, the number of publications, etc.

2.1 Student Training. Figure 1 shows the number of students financially supported by MRL and the number of degrees granted last year to such students. This number would be substantially increased if all students of MRL affiliated faculty members were included. Moreover, the existence of the MRL made possible the development of a new graduate major, Solid State Science, which in seven years grew to an enrollment of 75 students (without incorporating any of the traditional existing 'materials' degree programs such as metallurgy, ceramics or mechanics). This degree program now produces more Ph. D.'s annually than any other program on the campus except chemistry and physics. Figure 2 shows the growth in the number of publications by the faculty of the Laboratory, some 121 papers were published during the last twelve-month period.

2.2 Faculty. Materials Research Laboratory faculty continue to play an active role in the leadership of professional societies and other groups. Professor J. W. Faust, Jr. served on several committees of the Electrochemical Society; Professor Rustum Roy served as Chairman of the Basic Science Division of the American Ceramics Society; Professor L. E. Cross is Chairman of The Electrochemical Society Symposium on Ferroelectricity. Professor Roy has been serving as a member of the National Academy of Sciences Committee on Mineral Science and Technology, and Chairman of this Committee's Panel on Non-Metallic Materials which has just submitted its report and recommendations on the country's educational and research needs in this area. Professor W. B. White served on the Academies' MAB "Adhoc Committee on Infra-Red Transmitting Materials" and Professor Roy on the Adhoc Committee on Ceramic Processing. A major award for the best paper in ten years to Professors W. R. Buessem and L. E. Cross was announced by the Electronics Division of the American Ceramic Society, for their work on the physics of fine-grained barium

Total No. of graduate students receiving financial or research capability's support in M. R. L.	Full Support	-	88
	Partial	-	17
No. of undergraduate students involved:			
Summer Res. Interns			10
Part-time technical assistants			6
M. S. degrees granted			7
Ph. D. degrees granted			14

Figure 1.

M. R. L. SUPPORT OF STUDENT TRAINING

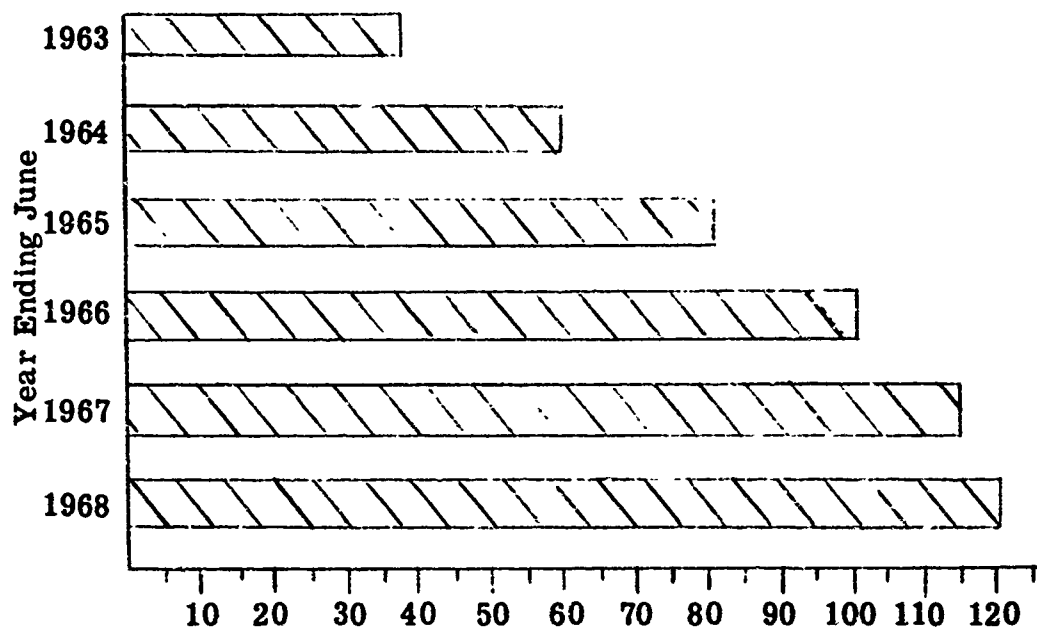


Figure 2.

RESEARCH PUBLICATIONS

titanate. Professors R. Roy and H. K. Henisch founded the *Materials Research Bulletin* (Pergamon Press) and have been acting as Co-Editors since its inception. The journal breaks new ground, partly by its subject-matter scope and partly by its publication speed (4 weeks, approximately).

Internally, three MRL faculty members assumed new administrative positions: Professor P. L. Walker was appointed Head of the newly-created Materials Science Department and Professor L. N. Mulay was made Head of the Solid State Science Section within that Department, and Professor A. Muan was appointed Head of the Department of Geochemistry and Mineralogy.

The Laboratory sustained a very severe blow by the untimely death of Professor Vladimir Vand, one of its senior members, whose brilliance and versatility were invaluable and are, indeed, irreplaceable.

- 2.3 Facilities. A new 70,000 sq. ft. building, designed by and for the Laboratory, is nearing completion and will be occupied probably by the 1st of January. Several smaller (\$10-20,000) items of capital equipment have been acquired from University funds during this year including a Princeton Applied Labs Vibrating Sample Magnetometer, additional x-ray diffraction and topography equipment, computer-interfacing equipment, etc.
- 2.4 Some Research Highlights. Among the research results which are likely to bear the most immediate technological fruit is one by Dr. D. M. Roy and her graduate student, Mr. S. P. Faile who, by incorporating up to several percent of H_2 in glasses under high pressure, have shown that this confers upon such glasses resistance to very heavy radiation dosages. The obvious application to solar cells is being actively followed up, and a study plan of the possible effect on semiconductors and integrated circuits themselves is now being formulated. Dr. Vedam and his associates have developed a new and versatile method, based on ellipsometry, for determining the optical constants of absorbing materials, even though these may be covered by thin films of foreign matter without the necessity for making any assumptions about the film. The work has already led to new values of the optical constants for Si, and measurements on Ge are in progress. Dr. Weber and co-workers have made important investigations in the structure and strength of inorganic materials of biological origin and have shown

that high-Mg calcite skeletal elements of echinoderms have an extraordinarily high strength-to-weight ratio, a fact which may have important incidental applications in the technology of composite materials. Dr. Henisch and his group have developed pyroelectric methods of radiation dosimetry and have carried out studies on the nucleation of crystals in gels, demonstrating homogeneous nucleation, perhaps for the first time. Dr. Cross and co-workers have elucidated the electrical behavior of strontium titanate, a substance which has been under investigation for over 20 years and regarded as a potential ferroelectric material. It has been shown that it is in fact anti-ferroelectric and that the application of external electric fields switches it into a paraelectric state. A new material, gadolinium molybdate, has been shown to represent a completely new class of ferroelectrics which undergo a phase transition due to its elastic instability, rather than due to dielectric interaction of the Lorentz catastrophe type.

- 2.5 Research-Information Dissemination and 'Coupling'. The MRL has had an active concern from the time of its creation with developing methods for the effective dissemination of its research results and, on an even more general scale, for the interpretation of materials science to the public. This concern is currently discharged through several different mechanisms.

The Director serves as chairman of a consortium of the Materials Research Directors of six universities and Vice-President or Research Director of some ten major industries of the Commonwealth of Pennsylvania. This group, among other functions, organizes and executes an extensive year-round program of seminars, lectures, workshops under the auspices of the State Technical Services Act.

Under the same auspices, the MRL prepared last year a series of six half-hour TV programs on special aspects of modern materials science and engineering. These programs are available for general loan as video tapes and in the form of kinescope copies.

The MRL is part of a three-unit team working together on the physics and chemistry of glasses: our partners in this joint effort are the Naval Research Laboratory and Bausch and Lomb, Inc.

An Industrial Coupling Program has been in operation for some years, involving the Laboratory with some ten companies in an intensive exchange of research - information. Report dissemination, seminar discussions, the sharing of facilities, and personal contacts continue to be a most effective pattern for University-Industry interaction.

The Laboratory aided materially in the organization of the Second International Conference on the Characterization of Materials, held in Rochester in November 1967, and is serving as host for the Second International Silicon Carbide Conference in October 1968, and for a one-day Working Party on Crystal Growth in Gels (October 10, 1968).

3.0 SUMMARIES OF RESEARCH RESULTS

We present below short summaries describing the research being carried out in the laboratory. These summaries are grouped logically according to subject matter since this indicates the real, interdisciplinary nature of the tasks. Within each of the groupings, faculty from different backgrounds do, in fact, interact and work together. A particular faculty member's research may therefore appear under several different tasks, under the main headings:

3.1 Preparation of Materials

3.2 Characterization of Materials

3.3 Properties of Materials

3.4 Research on Glass

3.5 Solid State Bioscience and Geoscience

3.1

PREPARATION OF MATERIALS

The original ARPA contract was in support of this laboratory's strength in the thermodynamics, kinetics and synthetic inorganic research in high temperature materials. We continue to maintain a major activity in this area, although it is now balanced by proportional work in the other areas.

3.1.1 CRYSTAL CHEMISTRY AND PHASE EQUILIBRIA IN VARIABLE VALENCE SYSTEMS

PERSONNEL

Rustum Roy, Professor of Geochemistry and Director, Materials
Research Laboratory
William B. White, Associate Professor of Geochemistry
Jean-Claude Joubert, Visiting Research Associate
Olaf Muller, Research Associate, Solid State Science
Kenneth L. Keester, Graduate Assistant, Solid State Science
Gregory McCarthy, Graduate Assistant, Solid State Science
John S. Berkes, Graduate Assistant, Solid State Science
Fred Nagle, Visiting Summer College Teacher

OTHER SPONSORSHIP

U. S. Army Electronics Command (DA 28-043-AMC 01304E)
National Science Foundation (summer college teacher program)

RESEARCH REPORT

Synthesis of Ferromagnetic FeBO_3 . The stability of the compound FeBO_3 with the calcite structure and Fe_3BO_6 with norbergite structure has been determined. Magnetic measurements on polycrystalline FeBO_3 revealed the compound to be a weak ferromagnet with a high anisotropy field below 115°C . Infrared spectra were used to determine characteristic absorption bands of the independent (BO_3) and (BO_4) groups

Crystal Chemistry of Rare Earth-Iron Borates. Huntite structure compounds with the formula $\text{LnFe}_3\text{B}_4\text{O}_{12}$ ($\text{Ln} = \text{La}^{+++}$, Nd^{+++} , Sm^{+++} , Eu^{+++} , Gd^{+++} , Tb^{+++} , Dy^{+++} , Ho^{+++} , and Y^{+++}) have been synthesized. X-ray powder diffraction patterns and cell parameter data have been measured. The infrared spectrum confirms the triangular coordination of boron in these compounds.

Synthesis and Crystal Chemistry of Boracite. We attempted the preparation of boracite, $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}(\text{NIB})$ by hydrothermal synthesis. This compound exhibits the very rare property of being ferroelec-

tric and ferromagnetic at the same time, at temperatures below 67°K. After a long unsuccessful period, we have succeeded recently in determining the conditions (temperature, pressure, starting materials) allowing us to prepare the material as the principal phase. We hope to be able to obtain single crystals suitable for physical studies in the near future

Phase Equilibria in the Systems MeO-Cr₂O₃-O at High Oxygen Pressure (Me⁺⁺ = Mg⁺⁺, Ni⁺⁺, Cd⁺⁺). Phase equilibria have been determined for the three ternary systems NiO-Cr₂O₃-O₂, MgO-Cr₂O₃-O₂ and CdO-Cr₂O₃-O₂ over the range of 450 to 850° and oxygen pressures of 2 to 3,500 atmospheres

Only two intermediate phases were found in the nickel system: NiCrO₄ (CrVO₄ structure) and the spinel NiCr₂O₄. The magnesium and cadmium systems are similar in that they have three analogous phases: the low temperature α -MgCrO₄ and α -CdCrO₄ (both with the CrVO₄ structure), the high temperature β -MgCrO₄ and β -CdCrO₄ (both with the α -MnMoO₄ structure) and the spinels MgCr₂O₄ and CdCr₂O₄. The cadmium system contains an additional phase, Cd₂CrO₅, which is primitive monoclinic, space group C_{2h}⁵-P2₁/a

Formation and Stability of the Platinum and Rhodium Oxides at High Oxygen Pressures and the Structures of Pt₃O₄, β -PtO₂ and RhO₂. The systems Pt-O and Rh-O have been investigated at high pressures and temperatures. Three platinum oxide phases were found and their pO -T stabilities roughly defined. The hexagonal α -PtO₂ already described in the literature; a new phase, the orthorhombic β -PtO₂ (CaCl₂ structure with $a_0 = 4.486\text{\AA}$, $b_0 = 4.537\text{\AA}$ and $c_0 = 31.138\text{\AA}$); and the cubic Pt₃O₄ (Na_xPt₃O₄ structure with $a_0 = 5.585\text{\AA}$). β -PtO₂ and Pt₃O₄ are black, highly insoluble solids which can easily be synthesized in bulk at high oxygen pressures

In the system Rh-O we found (besides the already-known two Rh₂O₃ polymorphs) a new RhO₂ phase with the rutile structure, $a_0 = 4.489\text{\AA}$ and $c_0 = 3.090\text{\AA}$. RhO₂ is a black, easily synthesized solid which is highly insoluble even in hot aqua regia

"Goldschmidt radii" were derived for Rh⁴⁺ and Pt⁴⁺ and found to be 0.64 \AA and 0.66 \AA respectively

New Crystalline Phases in the System Gold-Oxygen. Two crystalline phases, tentatively labeled AuO_x (probably Au_2O_3) and AuO_y , have been found in the system Au-O at high oxygen pressures and temperatures below 230°C . Under similar conditions, a phase near the composition $\text{Na}_{0.5}\text{Au}_2\text{O}_3$ could be synthesized. A defect structure (related to the sphalerite type) has been tentatively proposed for $\text{Na}_{0.5}\text{Au}_2\text{O}_3$. It is suggested that AuO_x and $\text{Na}_{0.5}\text{Au}_2\text{O}_3$ are isostructural, with the Na-sites completely empty in AuO_x . $\text{Na}_{0.5}\text{Au}_2\text{O}_3$ and AuO_x are both primitive cubic with a probable space group of $T_d - \bar{P}4_3m$ and unit cell constants of $a_0 = 4.832\text{\AA}$ and $a_0 = 4.80\text{\AA}$ respectively. Neither AuO_x nor AuO_y has as yet been prepared free from metallic gold admixture; hence, the precise stoichiometry of these phases is still unknown. The most significant part of this work on the noble metals is that for the first time we are able to establish the fact that even Pt and Au have oxides which are thermodynamically stable under room temperature and pressure conditions. Thus most so-called noble metals must have an oxide film coating under most conditions where they have been thought to be metals.

The System Cr-O at High Oxygen Pressures Additional experiments have been performed in the temperature range $250\text{--}400^\circ\text{C}$ at oxygen pressures from 2000 to 3500 kbars. The object here is to locate two invariant points which mark the co-existence of $\text{Cr}_3\text{O}_8 + \text{Cr}_2\text{O}_5 + \text{Cr}_5\text{O}_{12}$ - vapor and $\text{Cr}_2\text{O}_5 + \text{Cr}_5\text{O}_{12} + \text{CrO}_2$ + vapor. These occur near $P_{\text{O}_2} = 2000$ bars and $T = 260^\circ\text{C}$ and 350°C respectively.

The System ZnO-PbO-O at High Oxygen Pressures Pressure-temperature phase relations for the Pb-Zn-O ternary system have been determined with oxygen pressures up to 2800 bars and temperatures to 750°C . Three new ternary compounds are shown to exist in this range. Univariant decomposition curves for ZnPbO_3 , PbZn_2O_4 , and ZnPb_2O_5 have been determined, stability increasing as listed, respectively. X-ray powder diffraction data have been obtained for all three phases. ZnPb_2O_5 is optically uniaxial negative and tetragonal with $a_0 = 5.36\text{\AA}$ and $c_0 = 21.0\text{\AA}$. Cell constants were obtained by single crystal analysis. As the other two phases cannot be obtained in crystals $>1\mu$, optical and single crystal data cannot be obtained; however, analytical indexing of PbZnO_3 powder data gave: tetragonal, $a_0 = 10.86\text{\AA}$, $c_0 = 3.92\text{\AA}$. This compound may be a size model-structure of NaZn(OH)_3 as their a_0 cell dimensions coincide identically. Pure phases cannot be obtained due to low reaction and decomposition

temperatures; however, phase assemblages do show bright yellow cathodoluminescence. Dielectric measurements also showed photoconductive response; however, the magnitude of response due to unreacted ZnO in the samples could not be determined

The System CdO-PbO-O at High Oxygen Pressures. In the Pb-Cd-O ternary system a 300 isobaric section shows two new compounds: CdPbO_3 , which exists up to c. a. 580°C , and Cd_2PbO_4 which is stable in excess of 820°C . Crystal structures are unknown, but Cd_2PbO_4 is isostructural with Cd_2SnO_4 . The analogous stannate of CdPbO_3 is not. Photoconductive properties are sought. As a starting material, lead hydroxide was prepared and was found to be photosensitive in the visible and UV regions. Reversible photosensitivity was demonstrated by storage in an H_2O atmosphere in darkness. The process is being studied by diffuse reflectance spectra. Excellent, but unindexed, powder data have been obtained. Gravimetric analysis suggests $5\text{PbO} \cdot 2\text{H}_2\text{O}$ as the chemical formula

Phase Relations in the System Eu-Ti-O. Phase relations in a portion of the system Eu-Ti-O have been investigated at 1400°C . The following compounds were located: $\text{Eu}_2\text{Ti}_2\text{O}_7$, Eu_2TiO_5 , Eu_2TiO_4 , $\text{Eu}_3\text{Ti}_2\text{O}_7$ and what is believed to be $\text{EuTi}_{12}\text{O}_{19}$. The existence of the compound $\text{Eu}_4\text{Ti}_3\text{O}_{10}$ was ascertained although it could not be prepared as an equilibrium phase at 1400°C . What was previously thought to be the unique composition EuTiO_3 has been shown actually to be an extensive solid solution

Phase Relations in the System Sr-Ti-O. The 1350°C isotherm of a portion of the system Sr-Ti-O bounded by $\text{SrO-TiO}_2\text{-Ti}$ has been investigated. A new compound whose composition is approximately $\text{SrO} \cdot 6\text{Ti}_2\text{O}_3$ was located in addition to the previously reported Sr_2TiO_4 , $\text{Sr}_3\text{Ti}_2\text{O}_7$ and SrTiO_3 . Another previously reported compound, $\text{Sr}_4\text{Ti}_3\text{O}_{10}$, does not exist as an equilibrium phase over the temperature range $900^\circ\text{-}1400^\circ\text{C}$. The perovskite SrTiO_3 forms a solid-solid solution with SrTiO_2 by substitution of Ti^{3+} for Ti^{4+} with an appropriate number of oxygen defects. The Sr:Ti ratio varies only slightly from a value of one for this solid solution and there is no apparent change in symmetry or cell edge. No significant substitution of Ti^{3+} for Ti^{4+} was noted for Sr_2TiO_4 and $\text{Sr}_3\text{Ti}_2\text{O}_7$

Phase Relations in the System $\text{LiBO}_3\text{-B}_2\text{O}_3\text{-NiO}$. Phase equilibria have been determined by standard quench methods of binary system

NiO-B₂O₃, the binary join Li₂O-B₂O₃-NiO and 3 other sections through the Li₂O-B₂O₃-NiO ternary. The only compounds observed are 3NiO·B₂O₃, 3NiO·2B₂O₃, and LiBO₃. Liquidus curves have been determined in section and the ternary phase boundaries and liquidus surface estimated.

Phase Relations in the System MgO-NiO-SiO₂. Phase equilibria are being studied by hydrothermal and dry quench techniques. The solubility limit of Mg_{1-x}Ni_xSiO₃ is at $x = .10$ at 1300°C. With a clinopyroxene structure. CaMg_{1-x}Ni_xSi₂O₆ with the diopside structure can be prepared from $x = 0$ to $x = 1$.

THESES, DEGREES GRANTED

O. Muller, Ph. D. in Solid State Science, 1968: "Crystal Chemistry of Compounds in the Systems: T-O, Ln₂O₃-ReO₂, MeO-CrO₃-O, Pt-O, and Au-O".

PAPERS PRESENTED

O. Muller and R. Roy, "Preliminary Investigations in the Systems Au-O, Rh-O, and Pt-O at High Oxygen Pressure", Basic Sci. Div., Amer. Ceram. Soc., Boston, October 1967.

PUBLICATIONS

J. C. Joubert, T. Shirk, W. B. White and R. Roy, "Stability, Infrared Spectrum and Magnetic Properties of FeBO₃", Mat. Res. Bull. 3, 671 (1968)

Olaf Muller and Rustum Roy, "Formation and Stability of the Platinum and Rhodium Oxides at High Oxygen Pressures and the Structures of Pt₃O₄, β -PtO₂ and RhO₂", to appear in J. Less-Comm. Metals 16, 129 (1968).

Olaf Muller, Rustum Roy and W. B. White, "Phase Equilibria in the Systems NiO-Cr₂O₃-O₂, MgO-Cr₂O₃-O₂ and CdO-Cr₂O₃-O₂ at High Oxygen Pressures", accepted for publication by the J. Am. Ceram. Soc.

Olaf Muller, William B. White and Rustum Roy, "X-Ray Diffraction Study of the Chromates of Nickel, Magnesium and Cadmium", submitted for publication to Z. Kristallogr.

Olaf Muller, William B. White and Rustum Roy, "Infrared Spectra of the Chromates of Magnesium, Nickel, and Cadmium", submitted for publication to Spectrochimica Acta.

3.1.2 MECHANISMS AND KINETICS OF MINERAL AND OXIDE REACTIONS

PERSONNEL

G. W. Brindley, Professor of Mineral Sciences
G. E. Lailach, Research Associate (visiting fellow)
A. Wiewiora, Visiting Fellow
A. N. Copp, Research Assistant
W. G. Staley, Graduate Student, Solid State Science
T. D. Thomson, Graduate Student, Organo-Geochemistry
Ranbir Bhalla, Graduate Student, Solid State Science
R. Wardle, Graduate Student, Solid State Science
D. B. Adam, Graduate Student, Solid State Science

OTHER SPONSORSHIP

National Science Foundation (GA626, GP 4450)
National Aeronautics and Space Administration (NGR 39-009-015
[subcontract])
Grants-in-aid: Basic, Inc., Cleveland, Ohio
Gulf Research Foundation, Pittsburgh, Pennsylvania
Chevron Research Co., LaHabra, California
The Pennsylvania State University, Central Fund for Research

RESEARCH REPORT

Oxide Reaction Studies. Attention has been given particularly to reactions between Al_2O_3 (corundum) and SiO_2 (cristobalite) at temperatures 1500-1550°C which are below the lowest eutectic temperature of the system which is given as 1590°C. Studies have been made with mixed powders of various grain sizes, with densely sintered powder compacts pressed together, and with single-crystal corundum pressed against sintered powdered cristobalite. In the mixed-powder studies, the total of crystalline phases coexisting during the reaction is less than, and sometimes considerably less than 100%, which suggests the formation of noncrystalline, or glassy material. Particularly when coarse-grained alumina is embedded in fine-grained cristobalite, considerable glassy phase is formed and this is confirmed by

optical examination. Microprobe observations indicate that the formation of mullite proceeds principally by penetration of silica into alumina. When the alumina grain size is small, mullite forms rapidly and less glassy phase appears.

When densely sintered powdered compacts are reacted, cristobalite penetrates between the corundum particles and an expansion of the cristobalite structure of the order of 1-2% has been observed by X-ray diffraction measurements. The formation of the glassy phase appears to be a precursor of mullite formation; the mullite is found principally adjacent to and within the alumina. When single-crystal alumina is used, penetration is much reduced, a zone of glassy material is observed and very little mullite is formed.

Crystalline Solutions in Periclase. Extensive solution in MgO without large scale creation of cation vacancies has been explored in reactions of the following kinds: (i) Mg R^{2+} , (ii) $2\text{Mg R}^+ + \text{R}^{3+}$, (iii) $3\text{Mg } 2\text{R}^+ + \text{R}^{4+}$, (iv) $4\text{Mg } 3\text{R}^+ + \text{R}^{5+}$. Solutions of types (ii), (iii), and (iv) have been formed only with $\text{R}^+ = \text{Li}^+$, and with $\text{R}^{3+} = \text{Al}$, Cr , Fe , Mn , with $\text{R}^{4+} = \text{Ti}^{4+}$ and with $\text{R}^{5+} = \text{Nb}^{5+}$. In the last case, it is better to consider MgO forming a solid solution in Li_3NbO_4 . The particular cations which form or do not form these solid solutions, and the extent of the solid solutions observed at 1100° , cannot be interpreted simply in terms of ionic sizes; covalent considerations appear to be involved.

Hydration Studies of CaO, MgO and Dead-Burned Dolomite. Attention has been devoted principally to well-sized powders of CaO, using crushed single crystal chips and a particle size range of 44μ , hydrated under conditions of controlled temperature (mainly $20-120^\circ\text{C}$) and controlled water vapor pressures (mainly 4.6-130 mm Hg). The results indicate that the reaction is phase-boundary limited, is controlled mainly by water vapor pressure, and within the temperature range studied is largely independent of the temperature.

Dehydroxylation and Rehydroxylation of Layer Silicate Minerals. In the year under review, pyrophyllite and margarite principally have been studied. Pyrophyllite, after dehydroxylation in vacuo within a temperature range around $650-900^\circ\text{C}$, forms a moderately well crystallized anhydride phase, which gives X-ray powder diagram which can be indexed on a unit cell significantly expanded with respect to that of the parent mineral. It is believed that the

modification of the octahedral sheet of the structure results in a relaxation of certain constraints present in the original structure. Margarite, a calcium mica, was expected to show even larger effects than pyrophyllite, but these were not observed. Instead, dehydroxylation and recrystallization seem to occur almost simultaneously and this may well be a consequence of the calcium ions in the structure. Other layer silicates are currently under consideration.

The Nature of Metakaolin Precision measurements on lattice parameters of metakaolin by single crystal electron diffraction have shown a significant relaxation of the kaolinite structure after loss of water from hydroxyl radicals in the structure. The establishment of this result modifies previously held concepts of the nature of metakaolin. It should be emphasized that X-ray diffraction analysis is inadequate for studying the structure of the kaolinite anhydride phase.

Organo-Silicate Studies Attention has been given to the absorption of a variety of organic compounds of biochemical interest (pyrimidines, purines, and nucleosides) by the expanding silicate mineral, montmorillonite, after saturation with the following cations: Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Fe^{3+} , and under a range of pH conditions, mainly pH 2-10. Absorption takes place principally by a cation exchange mechanism under acid conditions, and is governed largely by the pK_a values of the compounds studied, but molecular size and shape also are important as well as the nature and positions of functional groups on the organic molecules. Of particular interest has been the observation of absorption under alkaline conditions particularly by the transition metal cations; absorption of this kind arises from the formation of complexes between the cations and the organic molecules and is related to the nature of the molecules and especially to functional groups.

Absorption of simple neutral, polar organic molecules by a relatively well crystallized synthetic layer silicate has been oriented chiefly towards a study of the nature of alcohol-silicate complexes. The development of complexes sufficiently well ordered for Fourier syntheses of electron density from X-ray diffraction intensities has encountered considerable difficulties. The preparation of the complexes directly on the stage of the X-ray diffractometer has shown the feasibility of preparing suitable materials and current work is directed towards the study of the

normal alcohols, $C_1 - C_7$ Parallel thermogravimetric measurements give information on the thermal stability of the complexes, and the numbers of molecules absorbed per unit cell of the structure.

Intersalation of Kaolinite by Potassium Acetate. Previous work has indicated that the expansion of kaolinite by intersalation of potassium acetate decreases with increasing structural disorder of the mineral. It has also been suggested that intersalation can be used as a distinguishing criterion between order and disordered forms of the mineral. The present studies provide only a partial confirmation of these results; highly disordered forms of kaolinite with platy morphology have been shown to give almost complete intersalation. When a well crystallized kaolinite is intersalated then washed free of the salt, it becomes disordered and/or consists of much thinner domains than the original material. In this condition it can be easily re-intersalated. It still remains obscure why naturally disordered materials resist intersalation.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

None

PUBLICATIONS

- G. W. Brindley, "Ethylene Glycol and Glycerol Complexes of Smectites and Vermiculites", Clay Min. 6, 237 (1966).
- G. W. Brindley and T. D. Thompson, "Complexes of Benzene, Pyridine, and Piperidine 1, 3 - Substituted Propanes with a Synthetic Ca-Fluorhectorite", Clay Min. 6, 345 (1966).
- J. Mering and G. W. Brindley, "X-Ray Diffraction Band Profiles of Montmorillonite - Influence of Hydration and of the Exchangeable Cations", Clays and Clay Min. 15, 51 (1967).

- G. M. Poncelet and G. W. Brindley, "Experimental Formation of Kaolinite from Montmorillonite at Low Temperatures", *Am. Mineral* 52, 1161 (1967).
- T. D. Thompson, Sally A. Wentworth and G. W. Brindley, "Hydration States of an Expanded Phlogopite in Relation to Inter-layer Cations". *Clay Min.* 7, 43 (1967)
- P. J. Ficalora and G. W. Brindley, "Oxidation of Magnesiowustite Single Crystals: II Dependence on Temperature, Oxygen Pressure, and Crystal Composition", *J. Am. Ceram. Soc.* 50, 662 (1967).
- G. W. Brindley, B. N. Narahari Achar and J. H. Sharp, "Kinetics and Mechanism of Dehydroxylation Processes: II. Temperature and Vapor Pressure Dependence of Dehydroxylation of Serpentine", *Am. Mineral* 52, 1697 (1967).
- G. W. Brindley, "Nomenclature of Phyllosilicates, Geometry of Ideal Layers, and Bonding", pp. 1-25; "Silicate Swelling in Water and Inorganic Media", pp. 1-43; "Disorder in Phyllosilicates", pp. 1-33. Three chapters in Layer Silicates, published by American Geological Institute, Washington, D. C. (1967).

3.1.3

CHEMISTRY OF CEMENT

PERSONNEL

D. M. Roy, Senior Research Associate, Geochemistry
M. Grutzeck, Graduate Student, Geochemistry

OTHER SPONSORSHIP

National Science Foundation (GK-1154)

RESEARCH REPORT

Hydration of Cement Phases: Microstructure and Element Segregation. Existing electron microprobe techniques were modified and used to analyze the hydration products of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, Ca_3SiO_5 and a synthetic cement. Electron back scatter and elemental x-ray display data were used to follow the deterioration of crystals of the individual compounds with succeeding stages of hydration, to determine the distribution of the cations in the grains and hydrates forming under investigation, and also to follow the rate of hydration of aluminates and silicates, both individually and combined in a synthetic cement.

Elemental analysis data were obtained at one micron intervals with a stationary electron beam, which aided in identifying hydration compounds present. New data concerning the composition of the earliest hexagonal hydrates present in the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ water reaction were presented. It is expected that the methods used will be applied to the study of more complex cement hydration reactions.

THESES, DEGREES GRANTED

M. Grutzeck, M. S. in Geochemistry, 1968: "Microprobe Investigation of Portland Cement Hydrate".

PAPERS PRESENTED

None

PUBLICATIONS

- D. M. Roy and A. M. Johnson, "Investigations of Stabilities of Calcium Silicate Hydrates at Elevated Temperatures and Pressures", in Proceedings of Conference on Calcium Silicate Building Products, S. C. I. Special Publication, Society of Chemical Industry, London, pp. 114-121 (1967).

3.1.4 HIGH PRESSURE SYNTHESIS, EQUILIBRIA AND KINETICS

PERSONNEL

F. Dache, Associate Professor of Geochemistry
R. Roy, Professor of Geochemistry
A. Bobrowsky, Senior Research Associate, Solid State Engineering
H. E. Shull, Instructor, Engineering Mechanics
G. Vezzoli, Graduate Assistant, Solid State Science
R. Frushour, Graduate Assistant, Solid State Science
M. Bhardwaj, Graduate Assistant, Solid State Science

OTHER SPONSORSHIP

National Science Foundation (GK-1686X)

RESEARCH REPORT

Development of New Equipment. A monobloc chamber of nominal 2-inch inside diameter, has been operated successfully at internal nitrogen pressures up to 210,000 psi.

A cryogenic pressure chamber for use at liquid helium temperatures has been designed for measurement of elastic constants as a function of pressure and temperature.

Procurement has been in progress on a triple-purpose pressure unit: (i) measurements of electrical properties of materials at pressures up to 30 kilobars; (ii) measurements of optical properties of materials at intended pressures of 30 kilobars, and (iii) measurements of elastic properties of materials at intended pressures of 40 kilobars.

These pressures are in hydrostatic fluids, not in solids.

Equilibria and Kinetics in the Sulfur System. By static and dynamic methods including volumetric and electrical studies, the polymorphism, fusion curve, and high pressure liquid phase-changes in

sulfur have been elucidated. Nine new rapidly reversible high pressure forms of sulfur have been found and the phase boundaries of these and the previously reported 4.04\AA phase have been delineated. A kinetic study indicates that the 4.04\AA phase forms rapidly at high pressure above 300°C and slowly between 250°C and 290°C . The melting curve shows sharp changes in curvature at 10 kb, 250°C and at 20 kb, 350°C . A transition that is almost temperature independent was found in liquid sulfur at about 10 kb. The effect of pressure on the polymerization transition of sulfur was investigated by differential thermal analysis as the phase boundary between orthorhombic and monoclinic sulfur.

Investigations of the polymorphism of selenium and tellurium have indicated the existence of rapidly reversible high pressure polymorphs that can only be quenched by very rapid cooling and x-raying at dry ice conditions. The melting curve of tin has been re-studied and the boundary of a new high pressure tin phase has been delineated.

The Influence of Non-Hydrostaticity on Equilibria and Kinetics in High Pressure Reactions. Non-hydrostatic forces applied to polycrystalline samples have produced no reproducibly measureable change for the equilibrium pressure of the polymorphic phase change in RbCl, RbI, KCl and CdS. However, nonhydrostatic forces present in a simple piston-cylinder device have been shown to cause significant changes in the initial transformation pressure and the kinetics for single crystals oriented in the $[100]$, $[110]$ and $[111]$ for the cubic system and the a and c directions in the hexagonal system.

A qualitative study of the kinetics for these phase changes shows that the rate is favorably affected by pressure. The addition of water reduces the hysteresis in the alkali halide transitions and thus allows lower initial transition pressures. The rate is sufficiently slow at these pressures such that quantitative rate data can be obtained. Analysis of shockwave data shows that the pressures and temperatures reported for transition observed by this method need not correspond in any direct way with the statistically observed phase transitions.

It was found that the results of piston-anvil and piston-cylinder experiments compare favorably for the quartz-coesite transition if great care is taken during the experimental procedure.

Preparation of Non-Crystalline Phases by High Pressure Reactions. One of the novel ways in which various solids may be rendered non-crystalline is by low temperature trapping of the structure during the process of transformation from a metastable high pressure phase to a stable phase, by careful annealing at 1 atm. at very low temperatures. This procedure has been applied to Ge by annealing Ge-IV and Ge-III prepared at high pressures. Very poor yields of NCS-Ge have been obtained from Ge-II.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

- A. Bobrowsky, "Metalworking Under High Pressures", Annual Meeting, AIChE, Tampa, Florida, April 1968.

PUBLICATIONS

- A. Bobrowsky, "Metalworking Under High Static Pressures (Controlled-Ductility Forming)", Proceedings of the CIRP International Conference on Manufacturing Technology, September 1967.

3.1.5

PRODUCTION OF PLASMA
SYNTHESIZED POLYMERS

PERSONNEL

F. J. Vastola, Associate Professor of Materials Science
C. Brooks, Graduate Student, Solid State Science

OTHER SPONSORSHIP

None

RESEARCH REPORT

The production of hydrogen-carbon and hydrogen-carbon-silicon polymers from atomic species, generated in a microwave plasma, has been continued. With the hydrogen-carbon polymers it has not been possible to obtain materials with a hydrogen to carbon ratio greater than 1.6. The hydrogen-carbon-silicon polymers behave similarly in that the maximum hydrogen to carbon plus silicon ratio is also less than 1.6, thus indicating direct substitution of silicon for carbon in the structure.

Since the silicon to carbon is only dependent upon the atomic concentration of silicon and carbon in the plasma a continuous series of polymers with varying silicon to carbon ratios can be produced. The structure of these polymers is now being studied by IR adsorption and laser-mass spectrometry. The latter technique involves the use of a laser to pyrolyze the polymers in a mass spectrometer.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

None

PUBLICATIONS

None

3.1.6

CRYSTAL GROWTH

One of this laboratory's specializations is in developing the science of crystal growth. We have established a group of faculty each supervising several students in this area, so that there is now a steady production of Ph. D. -level research, not in the making of a particular crystal in order to make measurements on it, but in the physical chemistry of the growth itself. Our prominent role at the International Conference of Crystal Growth held in Birmingham, England, has already been noted.

3.1.6.1

GROWTH OF PURE CRYSTALS

PERSONNEL

J. W. Faust, Jr., Professor of Solid State Science
H. M. Liaw, Graduate Student, Solid State Science
S. Hayden, Graduate Student, Physics

OTHER SPONSORSHIP

None

RESEARCH REPORT

Vapor Growth of Magnesium. A special furnace was built for this work. The furnace consists of a stainless steel tube that can be rigidly attached to a high vacuum system. The furnace can be baked out to assure the highest vacuum. The magnesium charge material is placed in a tantalum liner. A great deal of time was spent getting a suitable thermal gradient. Initial attempts to grow a crystal without a seed proved of little value. Since extreme purity is required special magnesium was obtained. Unfortunately the oxygen content is quite high and this has proved troublesome. When a seed was used growth resulted. Metallographic examination of the sample showed columnar growth indicating the temperature gradient was too high. It has been necessary to build a special temperature control to improve the thermal stability. A run is in progress using a number of seeds. The results from this run will help to determine the proper temperature difference.

Studies of Lead Dendrites The growth of lead dendrites has been studied by three techniques: (i) gel growth, (ii) growth from aqueous solutions, and (iii) electrodeposition. The gel growth was a sodium silicate with lead acetate. At first zinc was used to supply the driving force. The growth rate was determined by using a special rectangular container quite thin that would fit under a microscope. Other metals higher in the emf series than lead were used to determine if the magnitude of the emf difference change either the morphology or the rate. Some differences were found but no pattern has been found yet. The growth rates followed

a parabolic growth law. No change in the pH was found during growth. The dendrites were cross sectioned and examined metallographically as well as by X-rays. The main facets are (111), and the dendrites were found to be twinned.

When water was used in place of the gel, very fine dendrites grew. They had the appearance of being whiskers. The growth kinetics in the electro-deposition of lead are just getting started. The dendrites are quite similar in appearance to those grown by the gel method. Faceting is definitely (111) but neither twinning nor growth direction have been determined.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

None

PUBLICATIONS

J. W. Faust, Jr., F. Ogburn, D. Kahan and A. W. Ruff, Jr.,
"Twin Configurations in f. c. c. Dendrites", J. Electrochem.
Soc. 114, 1311 (1967).

3.1.6.2

CRYSTAL GROWTH IN GELS

PERSONNEL

H. K. Henisch, Professor of Applied Physics
E. S. Halberstadt, Senior Research Associate
J. Nickl, Research Associate
J. Perison, Research Assistant
S. Suri, Graduate Assistant, Solid State Science

OTHER SPONSORSHIP

Air Force Cambridge Research Laboratories (F19628-68-C-0109)

RESEARCH REPORT

The work has been concerned with two principal aspects of the project: the development of new growth methods and the control of nucleation. Under the first heading, a procedure for the growth of silver iodide crystals (plates, up to 12 mm diameter) has been developed. It makes use of the fact that AgI and KI can be complexed in solution and diffused into a reagent-free gel in this form. De-complexing sets in with increasing dilution, leading to nucleation and crystal growth. Experiments are also in progress on the growth of calcite crystals. Under the heading of nucleation studies, scanning electron microscope investigations have been carried out on vacuum-freeze-dried gels, and the resulting pictures related to observed nucleation rates. Consistent differences of structure and nucleation behavior can be correlated in this way, though not yet with high precision. Experiments are in progress on the effect of trace impurities and temperature gradients and a small book on the subject of crystal growth in gels is in preparation.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

- H. K. Henisch, "Crystal Growth in Gels", Solid State Physics Seminar, University of Kentucky, March 1968.
- H. K. Henisch, "Crystal Growth in Gels", Television presentations on Educational Network, Channel 3, June 1968.

PUBLICATIONS

- E. S. Halberstadt, "Growth of Single Crystals of Silver Iodide in Silica Gel", *Nature* 216, 574 (1967).
- E. S. Halberstadt and H. K. Henisch, "Recent Experiments on Crystal Growth in Gels", International Conference on Crystal Growth, Birmingham, England, July 1968.

3.1.6.3 HIGH TEMPERATURE SOLUTION (= FLUX) AND HIGH PRESSURE SOLUTION (= HYDROTHERMAL GROWTH)

PERSONNEL

R. Roy, Professor of Geochemistry
W. B. White, Associate Professor of Geochemistry
R. Garner, Graduate Assistant, Physics
J. F. Balascio, Graduate Assistant, Solid State Science

OTHER SPONSORSHIP

None

RESEARCH REPORT

Growth of Calcite. Attempts to grow calcite have been made hydrothermally in $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$ systems and with NaHCO_3 additions, by a flux technique using Li_2CO_3 as a solvent, and by flux pulling from a $\text{CaCO}_3\text{-Li}_2\text{CO}_3$ melt. The flux method yields crystals in the 1-5 mm size but separation of the crystals from the matrix remains a problem

Growth from Sulfide Fluxes. Work has been started on the growth of HgS from $\text{Na}_2\text{S-S-H}_2\text{O}$ melts. Liquidus temperatures in this system are low and one can find measurable solubilities of HgS in $\text{Na}_2\text{S-S}$ mixtures below the 300°C phase transition. Work thus far has been restricted to perfecting experimental techniques.

Review of Flux and Hydrothermal Growth. This review traces the recent developments of high temperature solution (flux) and high pressure solution (hydrothermal) crystal growth. High temperature solution (HTS) growth of oxide materials from ionic liquids (PbO , PbF_2 , Bi_2O_3 , KF and their combinations) and network-forming liquids (various borates for example) has advanced to the stage of a routine experimental tool. Recent significant improvements in technique include the use of controlled oxygen partial pressures to grow non-stoichiometric oxides and lower valence state oxides directly in equilibrium with a gas atmosphere, the use of moving flux zones modes to grow solid solutions, and the

use of isothermal flux-evaporation also to grow solid solutions. Current experimentation is directed toward improved understanding of the physical chemistry of the flux liquids (liquid structure and its influence on growth, location of crystallizing ions in the liquid structure, thermodynamic models for solution behavior, etc.) and toward the development of novel flux systems for non-oxide materials. High pressure solution (HPS) growth is less advanced as a routine technique because of difficulties with seed crystal surfaces and orientations, selection of workable solvents, and suppression of spontaneous nucleation and crystal flawing. Where these have been solved, however, much better material is grown by HPS methods than HTS methods in general. Research here is directed toward the discovery of useful non-aqueous solvents and a better understanding of the nature of the supercritical fluid and the growth process. HPS methods have very recently been used for growth of large single crystals of metastable phases by use of epitaxy on appropriate substrates.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

- R. Roy, "Recent Developments on Flux and Hydrothermal Growth", International Conference on Crystal Growth, Birmingham, England, July 1968.
- R. Roy and S. Theokritoff, "Growth of Metastable Phases by Low-Temperature Epitaxy", International Conference on Crystal Growth, Birmingham, England, July 1968.

PUBLICATIONS

- J. F. Balascio, W. B. White and R. Roy, "Growth of Single Crystal Hexagonal Selenium from Supercritical Ammonia", Mat. Res. Bull. 2, 913 (1967)

3.1.6.4 GROWTH OF METASTABLE PHASES

PERSONNEL

R. Roy, Professor of Geochemistry
S. Theokritoff, Graduate Student, Geochemistry

OTHER SPONSORSHIP

None

RESEARCH REPORT

Hexagonal GeO_2 . One of the most interesting and unexplored major areas of crystal growth theory and practice is the possibility of the controlled growth of large crystals of phases in environments where they are thermodynamically metastable. This problem is now receiving considerable attention in this laboratory. The first study has been an attempt to grow large crystals of the hexagonal quartz-structure form of GeO_2 on true epitaxial substrates of SiO_2 and AlPO_4 with the same structure. The high pressure solution methods are ideal for this purpose, and we have succeeded in growing cm size crystals of GeO_2 as overgrowths on SiO_2 (but not AlPO_4) from pure water at 100-200°C and less than 1000 bars.

Monoclinic Selenium. Following the success with GeO_2 , we have attempted to do the same thing with monoclinic Se overgrowing on various potential crystallographically selected epitaxial substrates, such as beryl, mica, Al_2O_3 , MgAl_2O_4 (in various orientations). CS_2 solutions at 200°C and saturation pressure have been used, with no success so far.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

R. Roy and S. Theokritoff, "Growth of Metastable Phases by Low-Temperature Epitaxy", International Conference on Crystal Growth, Birmingham, England, July 1968.

PUBLICATIONS

None

3.1.6.5 PREPARATION OF GRAPHITE CRYSTALS

PERSONNEL

P. L. Walker, Jr. . Professor of Materials Science
C. Roscoe, Assistant Professor of Fuel Science
J. J. Baker, Graduate Student, Fuel Science
D. Nagle, Graduate Student, Ceramic Science

OTHER SPONSORSHIP

Atomic Energy Commission (AT(30-1)-1710)
Airco Speer Fellowship

RESEARCH REPORT

The production of large single crystals of graphite by two techniques is being studied: (i) growth from iron and nickel melts, and (ii) growth from recrystallized pyrolytic graphite. Crystals are being characterized by gas phase etching techniques and gold evaporation. Crystals grown from iron melts are as defect-free as the best crystals yet seen - that is Ticonderoga graphite natural crystals. To obtain better crystals from recrystallized pyrolytic, it is concluded that the concentration of non-basal screw dislocations present in the as-grown material must be decreased.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

C. Roscoe and J. Baker, "Effect of Stress Recrystallization on Structure of Pyrolytic Graphite", US/UK Libby-Cockcroft Graphite Chemistry Meeting, Battelle-Northwest, May 1968.

C. Roscoe, "Microstructure of Melt-Grown Crystals", US/UK
Libby-Cockcroft Graphite Chemistry Meeting, Battelle-
Northwest, May 1968.

PUBLICATIONS

None

3. 1. 6. 6 MECHANISMS OF CRYSTAL GROWTH

PERSONNEL

W. B. White, Associate Professor of Geochemistry
R. Roy, Professor of Geochemistry
J. S. Berkes, Graduate Assistant, Solid State Science
M. S. Darrow, Graduate Assistant, Solid State Science
R. W. Hamaker, Graduate Assistant, Solid State Science

OTHER SPONSORSHIP

None

RESEARCH REPORT

Structure of Borate Flux Liquids. The nature of the alkali borate family of fluxes was examined by measuring the deviation of the solution from ideality utilizing NiO as a probe solute. Precise liquidus relations were determined for the systems NiO- $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, NiO- $\text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, and NiO- $\text{Rb}_2\text{O} \cdot 2\text{B}_2\text{O}_3$. The experimental liquidus curves were fitted to a model using regular solution theory. The deviations from ideal solution lead to a liquid model involving a di-borate molecular aggregate. The thermodynamic results were combined with results from optical spectroscopy to deduce the environment of the Ni^{++} ion in solution prior to crystallization. It was shown that Ni^{++} (and therefore by inference, other transition metal ions) is in a large network-modifying site with a very weak bonding to its surroundings. This situation accounts at least in part, for the behavior of the borates as crystal growth fluxes.

Microhardness of PbS-PbTe Solid Solutions. Vickers micro-indentation hardness as a function of composition has been measured for polycrystalline solutions of lead chalcogenide systems and results compared to exsolution tendencies as implied by subsolidus features of the phase diagrams. Each system exhibited a positive deviation from a linear hardness relation between the end member compounds. The most pronounced hardening was observed for PbS-PbTe solutions with maximum hardness occurring

at about 30 mole percent PbTe coincident with a large solvus with a critical composition at about 30 mole percent PbTe and approximately 805°C. The least amount of hardening was observed for the system PbS-PbSe which exhibits no exsolution as low as 300°C. The hardness versus composition curve was approximately symmetric about the 50 mole percent composition. Intermediate between these two systems, the PbSe-PbTe crystalline solutions exhibited an asymmetric hardness-composition curve with maximum hardness at about 30 mole percent PbTe. Partial phase studies indicate the possibility of a solvus maximum at 560°C to 600°C on the PbSe-rich side of the diagram.

Spinodal Phase Separation in PbS-PbTe Solid Solutions. The system PbS-PbTe exhibits a solvus with a critical temperature of 804°C. Controlled exsolution experiments have been conducted at temperatures below T_c at various compositions within and without the chemical spinodal curve. Replica electron micrographs and X-ray diffraction studies provide evidence for a spinodal decomposition mechanism in this ionic system.

Growth and Characterization of $Ga_xIn_{1-x}Sb$ Solid Solutions by TGZM. Temperature-gradient zone melting has been utilized to grow a wide range of solid solution compositions of $Ga_xIn_{1-x}Sb$ using indium and lead as zone metals. Single crystal growth was accomplished on {111} InSb seed substrates. Migration velocities as large as 12×10^{-7} cm/sec were observed during indium growth experiments, while velocities as large as 7×10^{-7} cm/sec were noted during lead growth experiments. All growth runs were performed with the top of the seed substrate at 420°C to provide a reference temperature for the migration experiments. Electron microprobe scans of sections taken along the growth direction have shown gradual increases in the concentration of GaSb in growth layers over the first 2 to 3 mm of solid solution growth. Thereafter, uniform compositional growth is indicated. Photomicrographs of growth surfaces have clearly indicated that growth proceeded by a two-dimensional nucleation mechanism. Etch pit observations taken along the growth direction have indicated noticeable decreases in the dislocation densities of the individual growth layers compared with those in the respective seed substrates.

Growth of Chalcogenides by TGZM. Attempts have been made to grow ZnSe and $ZnSe_yS_{1-y}$ by temperature-gradient zone melting. Both single crystals of ZnSe and CdS have been used as seed sub-

strates. Indium, lead and tin have been used as zone metals. Initially, growth experiments were conducted in an evacuated chamber at temperatures below 500°C; however, no zone motion occurred in any of the growth runs. Above this temperature range, evaporation from the molten zones necessitated the use of sealed ampoules with internal hydrostatic pressures of argon (~10 mm Hg). In growth experiments where lead or indium were used as the zone solvent, migration occurred at temperatures above 600°C. However, what initially appeared to be bulk migration was found to be surface migration of the metals away from the region of the zone.

THESES, DEGREES GRANTED

- J. S. Berkes, Ph. D. in Solid State Science, 1968: "Structure of Ni^{++} -containing Borate Fluxes from Crystal Field and Thermodynamic Considerations".
- M. S. Darrow, Ph. D. in Solid State Science, 1968: "Lead Chalcogenide Crystalline Solutions: Phase Equilibria, Mechanisms of Phase Separation and Micro-indentation Hardness Studies".
- R. W. Hamaker, Ph. D. in Solid State Science, 1968: "Mechanism and Characterization Studies of the Growth of InSb , $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ and ZnSe by Temperature-Gradient Zone Melting".

PAPERS PRESENTED

- J. S. Berkes and W. B. White, "Solution Behavior in the System $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ - NiO , $\text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ - NiO , and $\text{Rb}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ - NiO ", Basic Sci. Div., Amer. Ceram. Soc., Boston, October 1967.
- M. S. Darrow, W. P. White and R. Roy, "Microhardness of Polycrystalline Solid Solutions of Lead Chalcogenides", Amer. Ceram. Soc., Chicago, April 1968.

PUBLICATIONS

- R. W. Hamaker and W. B. White, "Mechanism of Single Crystal Growth in InSb Using Temperature Gradient Zone Melting", J. Appl. Phys. 39, 1758 (1968)

3.1.6.7 CRYSTAL GROWTH OF APATITE

PERSONNEL

D. M. Roy, Senior Research Associate in Geochemistry
R. Roy, Professor of Geochemistry
V. Caslavská, Research Associate, Solid State Science
A. Turner, Visiting Undergraduate Research Participation Student

OTHER SPONSORSHIP

None

RESEARCH REPORT

Gel and Flux Methods. Investigation has been initiated on the growth of single crystals of hydroxyapatite using two different techniques: the growth from gels under normal conditions and the growth from fused $\text{Ca}(\text{OH})_2$ solutions at elevated pressures.

Diffusion into Natural Crystals. Attempts were made to convert a natural single crystal of a Brazilian apatite cut in 1 x 4 x 4 mm blocks (with the c axis parallel with one of its walls) into the pure end (F, Cl or OH) apatites by holding the plates in molten salts with high concentrations of the chemical ions. The chemical composition of the original apatite showed concentrations of F = 4.75%, Cl = 0.73%, lattice parameter: $a = 9.39\text{\AA}$, $c = 6.88\text{\AA}$. Infrared absorption showed only a small amount of OH groups present. The effort to replace the $(\text{OH})^-$ and $(\text{Cl})^-$ groups by F^- was unsuccessful in spite of the thermodynamic probability of the chemical reactions used, and literature data on the success in conversion of powdered apatites (typically with CaF_2 at $\sim 800^\circ$). The electron microprobe analysis did not even register any change in composition in directions perpendicular to the surfaces of the crystals. The long-range experiments in aqueous solutions of various fluorides also did not show any progress in the desired direction. The fluoride melts used resulted in rapid chemical attack on the crystal. By means of hydrothermal treatment the content of OH groups was increased subsequently but complete

conversion was not achieved. Even in such samples, however, the electron probe indicated no change in the Cl distribution, suggesting more complex substitution relations among the anions than has been previously predicted.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

None

PUBLICATIONS

None

3.1.6.8 VAPOR GROWTH: CONCENTRATED CRYSTALLINE SOLUTIONS

PERSONNEL

R. Roy, Professor of Geochemistry
V. Caslavsky, Research Associate, Solid State Science
R. F. Messier, Graduate Student, Solid State Science

OTHER SPONSORSHIP

None

RESEARCH REPORT

CVD Growth of SnO₂ on Rutile Single Crystal Substrates. The vapor reaction deposition (VRD) growth technique previously used for NaCl, spinel and garnet phases was used to study SnO₂ crystal structure orientation dependence on a host substrate lattice (for which rutile single crystals were used). The reaction between SnI₄ and H₂O was used to grow on a TiO₂ substrate, which temperature was changed from 450-650°C. The reaction took place in a silica tube with the temperature of both the chemical substances and the substrate varying in the range 450-650°C. The rate of deposition could be changed and controlled by means of variations of the SnI₄ temperature and a system of stopcocks joined to the vacuum pump. The substrate surface orientation was perpendicular to the c axis; its surface was prepared by mechanical polishing down to 1 μ diamond paste and the etching in dilute HF for several seconds. The epitaxial films obtained were examined by optical microscopy, and X-ray and electron microscopy techniques to determine the quality of the SnO₂ layer. The thickness was measured from an electron backscatter image obtained in an APL EMX-20 electron microprobe analyzer.

Single crystalline SnO₂ films about 3 μ thick could only be obtained in a narrow range of reaction conditions with an extremely low deposition rate. In all other cases a poorly formed film with grain boundaries, imperfections and block misorientations was obtained. Increasing deposition rates invariably produced a polycrystalline film.

Growth of Concentrated Crystalline Solutions: Chromium Vapor Deposition, Oxidation and Subsequent High Temperature Diffusion Studies With Al_2O_3 Substrates. The objective of this study was to attempt to prepare 'ruby' crystalline solutions, which would be more homogeneous with respect to Cr^{3+} distribution than typical rubies, and in the process to generalize observations on use of diffusion methods to prepare concentrated crystalline solutions.

Thin wafers of clear sapphire (Al_2O_3) were sliced parallel to the boule axis to thicknesses of 0.5 to 0.75 mm. Pure Cr (99.99%) metal was then flash-evaporated onto both sides of polished and unpolished Al_2O_3 wafers maintained in ultra-high vacua ($<10^{-8}$ Torr) at $\sim 25^\circ\text{C}$. The Cr films were 2-3 μ thick.

Next, the samples were oxidized in air at 950°C for 15-20 hours, and finally high temperature diffusion of samples was conducted from 1700 - 1795°C and from 15 to 45 hours in duration in air-argon atmospheres. The sample, during the diffusion, was sandwiched between two other Al_2O_3 wafers which had Cr_2O_3 thin films on the side touching the sample.

The films of Cr evaporated on polished Al_2O_3 surfaces did not adhere well. Therefore, in most of the experiments conducted, the samples used had Cr films on unpolished Al_2O_3 .

X-ray diffraction showed the (110) planes of Cr parallel to the surface of the Al_2O_3 , and further, after oxidation of the chromium, it was found that the (110) plane of Cr_2O_3 was parallel to the substrate surface. Similar results have been reported by Sailors, et al.

The diffusion of the Cr_2O_3 into the Al_2O_3 lattice was not very successful. Diffusion at 1700°C for 19 hours showed that the Cr concentration ranged from 3% (at the edge) to 0% (20 μ in from the surface) as shown by electron microprobe analysis. Another sample diffused at 1795°C for 45 hours gave values ranging from 101/2% at the surface to 0% 25 μ in from the surface. Increase in time and temperature did not substantially increase the penetration depth of the Cr.

While in our previous study reasonable homogeneity of Cr_2O_3 was obtained in MgO substrates 1/2 mm thick, it is clear that such a method for Cr^{3+} doping of Al_2O_3 is impractical.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

None

PUBLICATIONS

None

3.1.6.9 HYDROTHERMAL GROWTH AND POLYTYPISM OF ZnS

PERSONNEL

H. L. Barnes, Professor of Geochemistry
S. D. Scott, Graduate Assistant, Geochemistry

OTHER SPONSORSHIP

None

RESEARCH REPORT

This comprehensive study of the pH, eH, pH_2O , T control on the solubility of ZnS in various alkaline systems is now complete and the results available as a Ph. D. thesis. Among the most significant findings are the conditions for controlled growth of a single polytype (e. g. 4H, or the end members 2H and 3C), and the finding that the transformation temperature of 3C, 2H is very strongly dependent on the S^{2-} activity. Thus it may be lowered from the usual 1050°C to near 400°C in solutions with very low S^{2-} activity.

THESES, DEGREES GRANTED

S. D. Scott, Ph. D. in Geochemistry, 1968: "Stoichiometry and Phase Changes in ZnS".

PAPERS PRESENTED

S. D. Scott and H. L. Barnes, "Non-Stoichiometric Phase Changes in Sphalerite and Wurtzite", Min. Soc. of Amer., Kingston, Canada, August 1967.

S. D. Scott and H. L. Barnes, "Sphalerite Geothermometry at $300^\circ\text{-}580^\circ\text{C}$ ", Geol. Soc. Amer., New Orleans, November 1967.

PUBLICATIONS

None

3.1.7

CORROSION STUDIES

PERSONNEL

R. Roy, Professor of Geochemistry
F. Dache, Associate Professor of Geochemistry
H. B. Krause, Senior Research Associate, Solid State Science
E. W. White, Assistant Professor of Solid State Science
G. A. Savanick, Graduate Assistant, Solid State Science
P. Gigl, Graduate Assistant, Geochemistry

OTHER SPONSORSHIP

Office of Naval Research (N00014-67-A-0385-002)

RESEARCH REPORT

Controlled Preparation of Oxide-Hydroxide Layers. An extensive program is underway to systematically produce oxide-hydroxide layers on pure metal single crystals under controlled conditions T, pO_2 , pH_2O and time. The object is to override normal surface conditions and reproducibly develop desired phases on various metals. A variety of techniques involving the electron probe, X-ray spectroscopy and scanning electron microscope are being developed for complete characterization of the surface layers. From these techniques we are becoming able to characterize the layers in terms of morphology, pore structure, chemistry - including valences, and the short and long range order. It is possible, simply from the oxygen and aluminum X-ray spectra, to identify corrosion layers on aluminum.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

E. W. White and G. A. Savanick, "Characterization of Non-Uniform Surface Layers", Symposium on Surface Character-

ization, Society for Applied Spectroscopy meeting, Chicago,
May 1968.

PUBLICATIONS

None

3.2

CHARACTERIZATION OF MATERIALS

The word characterization means many different things to different people. Yet a national committee (MAB Report 229-M) of materials scientists has pointed to the absence of sufficient "characterization" of a solid as one of the major obstacles to progress in materials science. We shall use their definition of characterization, to define the scope of this section.

"Characterization describes those features of the composition and structure (including defects) of a (ceramic) material that are significant for a particular preparation, a study of properties, or use, and suffice for the reproduction of the material."

We will, therefore, include only those studies which lead directly to the definition of the nature (chemical composition) location and arrangement (structure) of the atoms or ions in a solid.

3.2.1

CRYSTALLOGRAPHY

PERSONNEL

R E Newnham, Associate Professor of Solid State Science
 J. W. McCauley, Research Assistant, Solid State Science
 J F Dorrian, Graduate Assistant, Solid State Science
 H. S. Yoon, Graduate Assistant, Solid State Science
 R. W. Wolfe, Graduate Assistant, Solid State Science
 J A Malone Jr, Graduate Assistant, Solid State Science

OTHER SPONSORSHIP

Department of the Army (DA-19-006 AMC-325(X))
 Department of the Air Force (F33615-67-C-1427)
 Office of Naval Research (Nonr 656-(27))

RESEARCH REPORT

Dielectrics. Mixed bismuth titanate ferroelectrics possess layer lattices and micaceous morphology. Crystals are readily grown by flux methods. The generalized chemical formula for these compounds is $M_{n+1}X_mO_{3m+3}$, where $M = Bi^{3+}, Pb^{2+}, Na^+, K^+, Ba^{2+}, Sr^{2+}, Ca^{2+}$; $X = Ti^{4+}, Nb^{5+}, Ta^{5+}, Ga^{3+}, Fe^{3+}$; and $m = 2, 3, 4, 5$. m denotes consecutive perovskite layers along c , the crystallographic direction perpendicular to the layers. A simple X-ray test has been devised to identify small single crystals with different m values such as $BaBi_4Ti_4O_{15}$ and $Ba_2Bi_4Ti_5O_{18}$. The intensities derived from these experiments can also be used to determine cation ordering. In $Na_{0.5}Bi_{1.5}Ti_4O_{15}$, for example, structure factor calculations showed that sodium substitutes for bismuth in the perovskite layers, but not in the bismuth oxide layers.

Related ferroelectrics in the family $Bi_{4-x}R_xTi_3O_{12}$ ($R =$ rare earth) have been prepared as ceramics and single crystals. The solid solution limit increases with ionic radius: x_{max} approaches zero for the small Lu^{3+} and Yb^{3+} ions but exceeds 2 for La^{3+} and Pr^{3+} , showing that the Bi_2O_2 layer is not inviolate. The larger rare earth ions tend to stabilize the paraelectric phase; Pr^{3+} de-

presses T_c far more rapidly than Er^{3+} . Transition temperatures have been determined by DTA and dielectric measurements.

As m increases the bismuth oxide layers become further apart, and the structure more nearly approximates a simple perovskite. We are attempting to synthesize ferroelectrics with large m values, beginning with the series $Bi_{m+1}(Ti, Fe, Cr)_mO_{3m+3}$.

Detailed structure analyses of Li_2TiO_3 and ferroelectric $Bi_4Ti_3O_{12}$ are in progress. Intensity data for nearly 500 reflections were collected for a single-domain bismuth titanate crystal. Neither the intensities nor the angles showed appreciable deviation from orthorhombic symmetry, though physical measurements are consistent with monoclinic point group m . A class of weak reflections were observed which violate the systematic extinction conditions for the space group $Fmmm$ reported by Aurivillius. The diffraction symbol is Bcb rather than F . Since $Bi_4Ti_3O_{12}$ is ferroelectric, the most likely space group is polar $B2cb$. Atomic coordinates were refined by least squares analysis of the X-ray intensity data.

The most interesting features of the structure are the sizeable ferroelectric motions. Bi and Ti shift along the nonpolar b -axis as well as along a . Oxygens contribute little to the Bragg reflection, and their coordinates were not accurately determined. Further measurements are in progress.

Crystals of Li_2TiO_3 were accidentally grown while attempting to synthesize lithium bismuth titanate. The structure was refined by X-ray diffraction, confirming its resemblance to sodium chloride.

Magnetics. The magnetic properties of the transition metal tellurates are being investigated in cooperation with other groups at Penn State and Grenoble. Neutron diffraction patterns of the trirutile compounds Fe_2TeO_6 and Cr_2TeO_6 were recorded by Mme. M. C. Montmory. Both are collinear antiferromagnetics at low temperatures, with antiferromagnetic exchange interactions across shared edges and shared corners. The magnetic structures differ only in spin direction: moments are aligned along the tetragonal c -axis in Fe_2TeO_6 , and perpendicular to c in chromium tellurate. Neel temperatures are 200 and 105°K for the iron and chromium salts, respectively. Fe_2TeO_6 susceptibility measurements by Dr. James Dehn show a broad maximum well above T_N , per-

haps indicative of local magnetic ordering or clustering effects. Ni_3TeO_6 and Mn_3TeO_6 are now under study

Micas General relationships between bulk mechanical properties and structure type have been reviewed for silicate minerals, and correlations between elastic stiffness moduli and the Si-O bonding arrangement was established. Layer silicates like mica are especially interesting because of their flexibility, a rarity among ionic solids. Fluoridated micas are acid resistant and stable at high temperatures. We have examined two of these synthetic micas in detail

Fluorophlogopite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$), a flexible synthetic mica has been compared to the brittle mica $\text{BaLiMg}_2\text{AlSi}_3\text{O}_{10}\text{F}_2$. Fluorophlogopite commonly occurs as a 1-M polytype, crystallizing in space group $C2/m$ with $a = 5.308$, $b = 9.183$, $c = 10.139\text{\AA}$, $\beta = 100.07^\circ$, and $Z = 2$. The structure was determined and refined to an R-factor of 6% by anisotropic least squares methods employing three-dimensional counter diffractometer data. A careful search using $N(Z)$ tests, difference Fourier maps and acentric space groups failed to reveal Al-Si ordering in the tetrahedral layer. Mean bond lengths are $(\text{Al-Si})-\text{O} = 1.64$, $\text{Mg}-(\text{O,F}) = 2.06$, and $\text{K-O} = 3.14\text{\AA}$. The fluorophlogopite structure departs only slightly from the ideal mica layer, with a tetrahedral rotation angle of 6° .

Barium lithium fluormica is also a 1-M polytype with a slightly smaller cell $a = 5.286$, $b = 9.158$, $c = 10.038\text{\AA}$, $\beta = 100.12^\circ$. Least squares refinement of the coordinates and temperature factors gave an R-factor of 7% for 500 reflections. No long-range order occurs in either octahedral or tetrahedral sites, and the mean bond lengths are nearly identical to fluorophlogopite. Substitution of divalent barium for potassium contracts the interlayer separation by 0.2\AA and distorts the SiO_4 tetrahedra. The stronger interlayer bonding leads to greater hardness and fewer stacking faults.

THESES, DEGREES GRANTED

E. P. Meagher Ph.D. in Mineralogy, 1967. "The Crystal Structure and Polymorphism of Cordierite"

PAPERS PRESENTED

- R. E. Newnham and E. P. Meagher, "Crystal Structure of Ni_3TeO_6 ", American Crystallographic Association Annual Meeting, Minneapolis, Minnesota, August 1967
- K. Vedam, R. E. Newnham, J. W. McCauley, J. Caslavsky and R. Roy, "Relation of Mechanical Properties to the Structure of Micas", Army Materials and Mechanics Research Center Symposium on Structural Ceramics, Chicago, Illinois, March 1968.
- J. W. McCauley and G. V. Gibbs, "Significance of Weighting Schemes in an Anisotropic Least Squares Refinement of a Ruby", Second Materials Research Symposium, National Bureau of Standards, Gaithersburg, Maryland, 1967
- J. W. McCauley, R. E. Newnham, K. Vedam and G. V. Gibbs, "Crystal Structure Analysis of Synthetic Fluorophlogopite", Geological Society of America Meeting, New Orleans November 1967

PUBLICATIONS

- R. E. Newnham, "Crystal Structure and Optical Properties of Pollucite", Am. Min. 52, 1515 (1967).
- R. E. Newnham, "Cation Ordering in $\text{Na}_{0.5}\text{Bi}_{1.5}\text{Ti}_4\text{O}_{15}$ ", Mat. Res. Bull. 2, 1041 (1967)
- M. C. Montmory, M. Belakhovsky, R. Chevalier and R. Newnham, "Etude par diffraction neutronique et effet Mossbauer du tellurate de fer Fe_2TeO_6 ", Solid State Comm. 6, 317 (1968).
- M. C. Montmory and R. Newnham, "Structures magnetiques des composes tri-rutiles Cr_2TeO_6 et Cr_2WO_6 ", Solid State Comm. 6, 323 (1968).

3.2 2

POLYTYPISM

PERSONNEL

V. Vand. Professor of Crystallography (deceased)

J. I. Hanoka. Research Associate. Solid State Science

OTHER SPONSORSHIP

None

RESEARCH REPORT

Polytypism in Lead Iodide Direct evidence that polytypes of this material are due to the presence of a silver-containing nuclei has now been obtained. An X-ray study of 26 crystals gel-grown in a silver-free environment showed only the 2H structure to be present, an analogous group of crystals grown in a gel with silver present exhibited at least 45% of the polytypes present >2H. All but one of the higher polytypes found showed intensity distributions which indicated that these polytypes are members of the same structure series. This suggests that a structural series in polytypism is due to epitaxial growth on different nuclei of the same substance (e.g. silver for PbI_2).

An optical microscopic study of gel-grown PbI_2 crystals as they grow in situ has shown clearly that macroscopic crystals grow by the dislocation mechanism. Screw dislocations were observed to form due to twist boundaries, crystal buckling and cracking, and by the presence of foreign nuclei, but only the latter would be expected to result in polytypes >2H.

Polytypism in Diamond A 2H and a 3R polytype have been reported in the literature but no higher polytypes have yet been found. A combined optical (birefringence) and X-ray study is now under way on a large number of small crystals in the hope of finding polytypes >2H.

THESES, DEGREES GRANTED

J. I. Hanoka, Ph. D. in Physics, 1967: "Polytypism in Lead Iodide and Its Interpretation According to the Epitaxial Theory".

PAPERS PRESENTED

J. I. Hanoka and V. Vand, "Further Studies in Lead Iodide Polytypism", American Physics Society Meeting, Washington, D. C., April 1968.

PUBLICATIONS

J. I. Hanoka and V. Vand, "Further Studies of Polytypism in Lead Iodide", J. Appl. Phys. (in preparation).

3.2.3 X-RAY AND OPTICAL CHARACTERIZATION OF AGGREGATES

PERSONNEL

H. A. McKinstry, Assistant Professor of Solid State Science
W. R. Stitt, Graduate Student, Solid State Science
D. R. Lundy, Graduate Student, Solid State Science
C. W. Gregg, Jr., Graduate Student, Physics
D. C. Miller, Graduate Student, Solid State Science
E. A. Margerum, Graduate Student, Solid State Science

OTHER SPONSORSHIP

Office of Naval Research (Nonr 656(27))
National Science Foundation (GP-3232)

RESEARCH REPORT

Microstrain and Domain Size Measurements. An experimental method was developed to determine when a polycrystalline sample is completely annealed. The broadening of X-ray diffraction peaks is assessed by using the peak-to-valley ratio of the $K\alpha_1$ and $K\alpha_2$ peaks at an appropriate angle. This quick and sensitive method provides an effective way to determine the proper sample to be used as the reference material in the deconvolution of broadened X-ray diffraction peaks.

The study of the shape of X-ray diffraction peaks from worked polycrystalline oxide materials indicates that measurable changes occur. The lattice parameter of some of the materials studied also changes with the degree of cold-working.

Effect of Physical and Thermal History on X-Ray Temperature Factor. The temperature factor in X-ray structure analysis is not independent of the thermal and physical history of a sample. Differences exist between cold-worked and annealed samples. There also seems to be evidence for anisotropy in the temperature factor even for cubic materials. Studies of these effects are still in progress.

Evaluation of Synthetic X-Ray Diffraction Profiles The instrumental broadening of X-ray diffraction peaks can be calculated by the convolution of the known aberration factors. When these results are compared with experimental curves having controlled experimental parameters, the agreement indicates that the technique is capable of accounting for changes in these parameters. But, there remains an additional factor that can be compensated for by assuming that the annealed samples still possess a residual strain.

High Precision Elastic Constant Measurements. The elastic constants of materials can be measured by an ultrasonic method. An electronic system with electrical feedback has been devised which has a precision capability in excess of one part in 10^7 . The apparatus is used for several other projects on 3rd order elastic constant studies. The temperature dependence of the 2nd order elastic constants of tellurium are being investigated.

Light Scattering Computations. The scattering amplitude functions appearing in Mie's theory may be expressed as a Fourier cosine series with the 'scattering angle' as the variable. The formulae for making the transformation from a set of Mie coefficients to the corresponding Fourier series have been derived. Tables of coefficients to effect the transformation have been computed using programs executed on an IBM 360 computer. The results are being applied to scattering by air bubbles in ruby crystals with radii in the range 1.0×10^{-3} micron to 1.0 micron at a frequency corresponding to the wavelength 6328\AA in vacuum. Computations of the coefficients of the transformed series are nearing completion.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

C. D. Crescovitch, V. S. Stubican and H. A. McKinstry, "Kinetics of Precipitation and X-Ray Strain Measurements in the System $\text{MgO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ ", Meeting of American Ceramic Society, Chicago, April 1968

PUBLICATIONS

- E. W. White, H. A. McKinstry and G. G. Johnson, Jr , "Computer Processing of SEM Images", 95-103, Scanning Electron Microscopy: The Instrument and its Application, Proceedings of Symposium at ITTRI, 1968
- F. F. Lange and H. A. McKinstry, "Numerical Technique for Aligning Crystals from Laue Photographs", Trans. Met. Soc. AIME 242, 341 (1968)

3.2.4 X-RAY EMISSION SPECTROSCOPY

PERSONNEL

E. W. White, Assistant Professor of Solid State Science
H. B. Krause, Research Associate, Solid State Science
W. Zeigler, Research Assistant

OTHER SPONSORSHIP

Office of Naval Research (N00014-67-A-0385-002)

RESEARCH REPORT

Oxygen X-Ray Emissions Band Shift Studies. With the availability of high quality clinocllore crystals ($2d = 28.36\text{\AA}$) an extensive study has been undertaken of the oxygen X-ray emission bands for some 50 selected oxides. Changes in the oxygen K-emission band are correlated with the type of valence electrons available in the metal and with the oxidation state of a given transition metal element. For example, it is possible with this technique to establish the stoichiometry of one micron thick oxide film on transition metals.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

None

PUBLICATIONS

None

3.2.5 X-RAY ABSORPTION SPECTROSCOPY

PERSONNEL

E. W. White, Assistant Professor of Solid State Science
J. T. Hach, NDEA Fellow, Solid State Science
W. D. Bromley, Graduate Assistant, Physics
A. S. Bhalla, Graduate Assistant, Solid State Science

OTHER SPONSORSHIP

Air Force Materials Laboratory (F33615-67-C1047)

RESEARCH REPORT

Extended X-Ray Absorption Fine Structure Obtained from Thick Targets A technique has been developed for observing the X-ray absorption edge fine structure directly in the continuum emission from electron bombarded thick targets. This allows one to study the extended fine structure from materials that cannot be prepared as uniform thin films.

Effect of Electrical Conductivity on Extended Fine Structure. Early investigators have noted the characteristic difference in absorption spectra from metals as compared with the same elements in compounds such as oxides. The question arises as to whether this difference might not be in some way attributed to the characteristically different electrical properties of the metals versus insulators. To test for any dependence on electrical conductivity two materials were chosen for study which undergo marked insulator \rightleftharpoons conductor transition with only minor changes in stoichiometry or structure. Stoichiometric TiO_2 is an insulator with a resistance of about 10^{12} ohm/cm as compared with $\text{TiO}_{1.98}$ having a resistivity of about one ohm/cm. VO_2 undergoes a reversible insulator \rightleftharpoons conductor transition at about 63°C with a relatively small structural rearrangement. The extended fine structure spectra for the Ti K absorption edge and the V K absorption edge were recorded but no significant differences were observed, hence it has been concluded that electrical conductivity is of no direct consequence in the study of extended fine structure.

Design and Construction of Vacuum Scanning Double Crystal Spectrometer Design and construction of the double crystal spectrometer is now completed and final tests and evaluations are underway. Included in the development were (i) vacuum enclosure, (ii) spectrometer motions for both crystals, (iii) temperature controlled crystal mountings, (iv) high intensity demountable X-ray tube, (v) high precision automated tangent arm drive, (vi) vacuum pumping system, (vii) high power (10 kV, 500 mA) fully stabilized X-ray generator and automated X-ray readout system. This instrument will be used to obtain high resolution leading edge X-ray absorption spectra in the soft X-ray range as well as high resolution X-ray emission band spectra to aid in our interpretation of spectra obtained in the higher speed single curved crystal spectrometer.

THESES, DEGREES GRANTED

- V. D. Bromley, M. S. in Physics, 1968: "Effect of Electrical Conductivity on Extended X-Ray Absorption Fine Structure".
- J. T. Hach, M. S. in Solid State Science 1968. "Study of Extended X-Ray Absorption Fine Structure Using Thick Samples".

PAPERS PRESENTED

- J. T. Hach and E. W. White, "Study of Extended X-Ray Absorption Fine Structures Using Thick Targets", Conference on Applications of X-Ray Analysis, Denver, August 1967

PUBLICATIONS

None

3.2.6 LASER-MASS SPECTROMETRIC STUDIES OF STRUCTURE AND CHEMISTRY

PERSONNEL

B. E. Knox, Assistant Professor of Solid State Science
S. D. Varney, Research Assistant
V. S. Ban, Graduate Student, Solid State Science
Y. T. Cho, Graduate Student, Solid State Science

OTHER SPONSORSHIP

NASA Institutional Grant to University (NGR-39-009-015)
National Science Foundation (GP-8584)

RESEARCH REPORT

Solid-Vapor Reactions of Surface Materials in Lunar Environments. As a part of a program studying lunar and planetary surfaces vaporization processes of naturally-occurring terrestrial silicates are being investigated. Pulsed ruby and neodymium-doped glass lasers are used to vaporize these materials in the ionization chamber of a time-of-flight mass spectrometer from which time-dependent mass analyses are obtained.

A series of silicates from the $\text{N}_2\text{-Si-O}$ system have been prepared and then vaporized in the mass spectrometer. A series of terrestrial silicates representing several pyroxenes, an amphibole, an olivine, an epidote, a garnet and a rhodonite have also been vaporized with the laser and analyzed. Dehydroxylation of several natural hydrous minerals have been studied, also, as well as the laser-induced removal of radiogenic gases from meteorites.

Development of the Laser-Mass Spectrometer as a Lunar Analysis Instrument. The objective of this program is to develop the techniques and basic instrumentation necessary to utilize the laser-mass spectrometer for lunar and planetary exploration. Basic studies aimed at understanding the mechanisms of laser-induced vaporization of solids are being conducted. In addition

studies of the laser vaporization of inorganic and organic heterogeneous "natural" materials and laser-induced desorption of adsorbed and occluded gasses as well as water are being conducted.

Two different vaporization processes result from the laser-solid interaction. The first occurs during the initial fast-rise energy pulse and produces a pressure wave that tends to fragment the solid and ionize products. The other results from the relatively long heating of the laser pulse during which time the solid is heated to its boiling point, the vapor species being produced by sublimation or boiling. The short-lived ions produced initially provide clues to the short range order structure of many amorphous materials, while the neutral species that boil or sublime from the solid represent substances in pseudo equilibrium at some high temperature.

The Laser-Mass Spectrometer for Chemical Analysis of Solids

The object of this study is to provide fundamental information on the laser-induced vaporization of pure elemental solid materials and simple binary and ternary compounds. The development of this instrument as a quantitative tool depends on understanding the mechanisms of vaporization and ionization which result from the high energy flux and short dwell time of a laser pulse. Information about the energy spread of the particles produced is also being sought. In addition both mass discrimination effects and laser-vapor cloud interactions are being studied.

Laser Vaporization of Group VA Oxides and Chalcogenides. The laser vaporization of antimony, arsenic, bismuth, selenium, and tellurium, plus their binary and ternary combinations and the oxides of arsenic, antimony and bismuth are being investigated with the time-of-flight mass spectrometer. Amorphous materials as well as crystalline compounds and solid solutions are being vaporized to investigate the relationship of the species in the vapor to the nature of the solid from which they were removed. In the case of the bismuth-selenium system SRO structure of the glassy compositions can be seen in the vapor. Structural effects have also been observed in the various polymorphs of arsenic and antimony oxide.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

- B. E. Knox, "Mass Spectrometric Study of the Laser-Induced Vaporization of Selenium and Various Selenides", International Spectrometry Conference, Berlin, September 1967.
- B. E. Knox and V. Ban, "Mass Spectrometric Study of the Laser-Induced Vaporization of Selenium and Various Selenides", invited paper, 9th Annual Time-of-Flight Mass Spectrometry Symposium, Cincinnati, Ohio, September 1967.
- B. E. Knox and J. Schottmiller, "Laser-Induced Vaporization of Bismuth-Selenium Alloys", Second International Conference on the Characterization of Materials, Rochester, November 1967.
- B. E. Knox and V. Ban, "Mass Spectrometric Studies of the Laser-Induced Vaporization of Arsenic and Various Arsenic Selenides", Sixteenth Annual Conference on Mass Spectrometry and Allied Topics, Pittsburgh, May 1968.

PUBLICATIONS

- B. E. Knox, "Mass Spectrometric Studies of Laser-Induced Vaporization I Selenium" Mat Res Bull 3, 329 (1968)
- B. E. Knox, V. Ban and J. Schottmiller, "Mass Spectrometric Studies of Laser-Induced Vaporization II The Bismuth-Selenium System", Mat Res Bull 3, 337 (1968)
- B. E. Knox, "Mass Spectrometric Study of the Laser-Induced Vaporization of Selenium and Various Selenides". Advances in Mass Spectrometry, Vol 4, pp 491-497 Institute of Petroleum, London 1968

3.2.7 CHARACTERIZATION BY IR AND OPTICAL SPECTROSCOPY

PERSONNEL

W. B. White, Associate Professor of Geochemistry
B. A. DeAngelis, Graduate Assistant, Solid State Science
P. Sitaram, Graduate Assistant, Solid State Science
R. K. Moore, Graduate Assistant, Geochemistry
J. F. Lewis, Visiting College Teacher
B. Braunstein, Undergraduate Assistant

OTHER SPONSORSHIP

National Science Foundation (GP-3232 and summer college teacher program)
Atomic Energy Commission (AT(30-1)-2581)

RESEARCH REPORT

Infrared Spectra and Order-Disorder in Spinels. Some details of the factor group method (used to analyze normal modes at the center of Brillouin zone) have been clarified. These include the choice of the unit cell for nonprimitive lattices and the distinction between symmorphic and nonsymmorphic space groups.

The symmetry coordinates for the spinel structure have been derived and used for the factorization of a secular determinant obtained by using a simplified potential including only the stretching of the bonds.

Single crystals of LiGa_5O_8 and ZnAl_2O_4 have been grown with the flux method; they have been oriented and polished for the purpose of taking Raman spectra. Single crystals of MgAl_2O_4 and $\text{MgO} \times 2.9\text{Al}_2\text{O}_3$, not grown in this laboratory, have been, also, oriented and polished for the same purpose.

The spectra of several compounds have been extended to the far infrared region (up to 300 microns) by using the IR 11 infrared spectrophotometer. The compounds taken into consideration

include some spinels (ZnAl_2O_4 , MgAl_2O_4 , MgCr_2O_4 , NiGa_2O_4 , ZnGa_2O_4) and ordered spinels like LiNbZnO_4 (1.1 order on tetrahedral sites) and $\text{Cr}_2\text{LiGaO}_8$ (1.1 order on octahedral sites).

Spectrum of Nd^{+++} in LaAlO_3 Good optical quality crystals of Nd:LaAlO_3 with the Nd content at 1% and 5% grown by Czochralski method were obtained from Union Carbide Corporation. These crystals are predominantly twinned along $\{100\}$ planes of the pseudo cube. X ray diffraction method is used in finding out the $\langle 111 \rangle$ direction of the pseudo cube. An effort has been made to detwin the crystals by applying a uniaxial stress on the lines suggested by Fay and Brandle [International Conference on Crystal Growth, Boston, June 1966]. For some unknown reason we could not succeed in detwinning the Nd-doped crystals (LaAlO_3) on an irreversible basis. A small device which can be incorporated in all the spectrometers is used to apply a uniaxial stress, at which the crystals are detwinned at room temperatures.

The Cary 14 model infrared spectrometer used to obtain the absorption spectra in the region 3000\AA to 26000\AA at room temperatures. Good quality polaroids were used to record the polarization features of the data. An effort is underway to repeat the data at liquid helium temperature.

The fluorescence spectra at room and liquid nitrogen temperatures were studied at Westinghouse Electric Corporation. Jarrel Ash 1 meter spectrometer and RCA 7102 photomultiplier detector served to obtain the fluorescence data. A 900-watt tungsten source and the appropriate Corning filters were used in these studies. Polaroids were used to obtain the polarization features of the transitions from the term $4F_{3/2}$ to the terms $4I_{9/2}$ and $4I_{11/2}$.

Optical Spectra of Transition Metals in Garnet The spectra of a number of natural garnets have been obtained in the range 0.35 to 3.5 microns. In the pyrospite garnets, the observed spectra are very complex. 12 bands can be assigned to Fe^{++} eight-fold coordination. The intensities and band widths allow the grouping of the bands into (i) three bands generally between 8,000 and 4,400 cm^{-1} arising from spin-allowed transitions within the $5D$ ground state and (ii) nine bands between 30,000 and 14,000 cm^{-1} arising from transitions between a quintet ground state and the low-lying triplet and/or singlet excited states. The large number of bands is due to the removal of all degeneracy by the crystal field of the

distorted (D_2-222) cube site in the garnet structure. There are small shifts in frequency associated with small changes in inter-atomic distances but otherwise the spectra retain a remarkable similarity from one pyroxene garnet to another.

In the ugrandite garnets, the observed spectra are much simpler and are due to Fe^{+2} in the trigonally-distorted octahedral (S_6-3) site. This simplicity is to be expected since all transitions are spin-forbidden and very few levels are available for transitions in the range of observation. Selection rules have been calculated for all transitions and an assignment of the bands has been made.

Optical Spectra of Iron in Pyroxenes The optical spectrum of ferrous iron in the pyroxene structures exhibits a complex group of spin-allowed bands. These bands have been interpreted by Bancroft and Burns as arising from an exceptionally high degree of splitting of the octahedral Fe^{+2} energy levels, caused by the extreme distortion of the cation sites in the various pyroxenes. To check these ideas further, optical spectra were obtained on an analyzed suite of natural hypersthene, pigeonite, salite, acmite, aegerine, synthetic clinopyroxenes, and synthetic members of the diopside-hedenbergite series. The effect of other ions on the spectra was examined in the diopside-hedenbergite series by the systematic substitution of Ti^{4+} and Al^{3+} into the structures. Bands appear in the regions of 13,000, 11,000, and 4000-5000 cm^{-1} . The arrangement of bands is most strongly controlled by the space-group symmetry of the structure. The effect of changing iron concentrations is mainly one of intensity, with only minor frequency shifts. The characteristic spectra of Fe^{+2} appear in the acmite and aegerine spectra, and also in some of the other pyroxenes, when induced by the substitution of Al^{+3} . The arrangement and frequency of the bands can be interpreted in terms of the geometry of the cation site.

IR Spectra of Chromates IR spectra have been determined for $NiCrO_4$, $\alpha-MgCrO_4$, $\alpha-CdCrO_4$ (all crystallizing with the $CrVO_4$ structure); $\beta-MgCrO_4$, $\beta-CdCrO_4$ (both with the $\alpha-MnMoO_4$ structure); and Cd_3CrO_5 . The number of bands is consistent with the predictions of a factor group analysis. It is shown that a dichromate-like spectrum can arise from chromate anions if the CrO_4 tetrahedron is sufficiently distorted.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

R. K. Moore and W. B. White, "Optical Spectra of Iron in Garnets", Amer. Mineral Assoc., Kingston, Ontario, September 1967.

PUBLICATIONS

W. B. White, R. Roy and J. McK. Crichton, "The Alexandrite Effect: An Optical Study", Amer. Mineral. 52, 867 (1967).

W. B. White and K. L. Keester, "Selection Rules and Assignments for the Spectra of Ferrous Iron in Pyroxenes", Amer. Mineral 52, 1508 (1967).

E. W. White and ... White, "Electron Microprobe and Optical Absorption Study of Kyanite", Science 158, 915 (1967).

W. B. White, "Diffuse Reflectance Spectra of Rare Earth Oxides", Appl. Spectros 21, 167 (1967)

3.2.8 ELLIPSOMETRIC CHARACTERIZATION OF FILMS ON SILICON

PERSONNEL

K. Vedam, Associate Professor of Solid State Science
F. Lukes, Visiting Senior Research Associate, Solid State Science
E. Schmidt, Visiting Research Associate, Solid State Science
R. Rai, Graduate Student, Solid State Science
W. Knausenberger, Graduate Student, Solid State Science

OTHER SPONSORSHIP

National Aeronautics and Space Administration (NCR-30-009-042)

RESEARCH REPORT

Before any investigation on the kinetics of oxidation of silicon by ellipsometry can be undertaken, the true optical parameters of silicon must be known. A new method has been developed by which it is now possible from a series of ellipsometric measurements, to obtain uniquely all the optical parameters of the system: absorbing substrate + non-absorbing surface film. The method utilizes the fact that the reflectivity of such a system remains essentially constant for a small but finite range of surface film thicknesses. Furthermore it hinges on the fact that the ellipsometric parameters Δ and ψ measured on different film thicknesses grown on the same sample, are compatible with only one unique choice of the parameters n_2 , k_2 , and n_1 . Measurements on chemically etched samples of silicon yield the values of the optical parameters as $n_2 = 4.052$ and $k_2 = 0.029$ in agreement with the results of earlier workers. The results on cleaved samples of silicon, on the other hand, reveal that the true values are $n_2 = 4.14_0$ and $k_2 = 0.03_4$ for $\lambda 5461\text{\AA}$.

THESES, DEGREES GRANTED

R. Rai, M. S. in Solid State Science, 1967: "Simultaneous Determination of Refractive Index and Thickness of Very Thin Films by Ellipsometry."

PAPERS PRESENTED

None

PUBLICATIONS

K. Vedam, R. Rai, F. Lukes and R. Srinivasan, "Simultaneous and Independent Determination of the Refractive Index and the Thickness of Thin Films by Ellipsometry", J. Opt. Soc. Amer. 58, 526 (1968).

3.2.9

ETCHING AND DEFECT STUDIES

PERSONNEL

J. W. Faust, Jr., Professor of Solid State Science
M. F. Ehman, Graduate Student, Solid State Science
G. Jindal, Graduate Student, Solid State Science
I. Kohatsu, Summer Student

OTHER SPONSORSHIP

None

RESEARCH REPORT

The Etching of Metals and Semiconductors. Work is in progress in tabulating all of the etchants for solid state investigations. In the area of etching research, the etching of germanium was studied using two different oxidizing agents and several complexing agents. The oxidizing agents were HNO_3 and H_2O_2 while the complexing agents were HF , tartaric acid, sucrose, H_2O , citric acid, manitol and oxalic acid. Microscopic examination showed that for a given oxidizing agent the type of attack was similar but different for another oxidizing agent. Furthermore the activation energies for the two oxidizing agent series were different. This suggests that the oxidizing agent controls the mode of attack. Comparing the complexing agents it was found that the activation energies were the same for any given oxidizing agent but that the etch rates were different. This suggests that the complexing agent determines the rate of attack.

Defect Studies in Germanium. Studies were started on a project to study microdefects in germanium. The time was spent learning to thin samples for transmission electron microscopy. A special jet etcher was built that appears to give satisfactory results.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

J. W. Faust, Jr., "Studies on Surface Preparation", Symposium on Semiconductor Surfaces, American Chemical Society Meeting, San Francisco, May 1968.

PUBLICATIONS

- A. Sagar, W. Lehman and J. W. Faust, Jr., "Etchants for ZnSe", J Appl. Phys. 39, (October issue) (1968).
- A. Sagar and J W. Faust, Jr., "Observations of Dislocations Piled up Against a Low Angle Boundary on Bi₂Te₃", J. Appl Phys. 38, 2410 (1967).
- A. Sagar and J. W. Faust, Jr., "Investigation of Cu Diffusion in Bi₂Te₃ by Etching Technique", J. Appl. Phys. 38, 3479 (1967).

3.2.10 ELECTRON MICROSCOPY OF DEFECTS

PERSONNEL

R. Queeney, Assistant Professor of Engineering Mechanics
M. Immar, Associate Professor of Materials Science
L. Peterson, Graduate Student, Engineering Mechanics

OTHER SPONSORSHIP

National Science Foundation Institutional Grant

RESEARCH REPORT

Intersections of coherent twin boundaries and high-angle grain boundaries in thin films of copper and copper-zinc alloys, the latter containing less than 30% zinc by weight, were examined in transmission electron microscopy. Photomicrographs of these intersections provided data which, in turn, gave the ratio of twin boundary Helmholtz free energy to grain boundary Helmholtz free energy.

The electron microscopic techniques used included the correlation of diffraction patterns with coherent twin boundary directions to determine twin boundary and grain boundary plane orientations. In addition, the analysis of Kikuchi line diffraction patterns was utilized, whenever possible, to more accurately determine the orientation of the metal foil relative to the electron beam.

The techniques described appear to provide average interfacial free energy ratios approximately 30% different from previous optical measurements. The variation in interfacial free energy ratios is halved, moreover, using electron microscopic techniques: in particular, negative ratios, indicating negative free energies, are eliminated.

The mean ratios of twin boundary free energy to grain boundary free energy were found to be 0.034, 0.032, 0.031, 0.029, and 0.023 for pure copper, copper-5% zinc, copper-10% zinc,

copper-20% zinc, and copper-30% zinc, respectively. All measurements were taken on specimens quenched from 875°C.

It was also found that, for a copper-30% zinc alloy, the mean ratio of twin boundary free energy to grain boundary free energy increased as annealing time increased. This result indicates that the elimination of high-energy grain boundaries may act as a stimulus to grain growth.

Finally, utilizing the mean ratio of twin boundary free energy to grain boundary free energy for pure copper and the well-established average high-angle grain boundary free energy for pure copper of 613 ergs/cm², the twin boundary free energy of pure copper was computed to be 21 ergs/cm².

THESES. DEGREES GRANTED

None

PAPERS PRESENTED

M. Inman and R. Queeney, "Relative Interfacial Free Energies in Copper and Copper-Zinc Solid Solutions", Annual Meeting, AIME, New York, February 1968

PUBLICATIONS

M. Inman and R. Queeney, "Stacking Fault Energy in Pure Copper", submitted to Acta Met

L. Peterson and R. Queeney, "Interfacial Energies of Dislocation Arrays", submitted to Acta Met

3.2.11 SCANNING ELECTRON MICROSCOPY

PERSONNEL

E. W. White, Assistant Professor of Solid State Science
G. G. Johnson, Jr., Assistant Professor of Computer Science
H. A. McKinstry, Assistant Professor of Solid State Science
R. Roy, Professor of Geochemistry

OTHER SPONSORSHIP

None

RESEARCH REPORT

Routine Evaluation The SEM, now in operation for one year, has been used on a wide variety of problems such as studies of precipitation in glass, surface oxidation of metals, structure of silica gels and some work with biological tissues and micro-organisms. We find the instrument to be quite serviceable and simple enough to operate so that several persons now operate it routinely in their research. A general survey of the SEM application to ceramics has been presented by White and Roy (see reference below)

Computer Processing of SEM Images The SEM analog signal is ideally suited to digital recording and subsequent computer processing for rapid quantitative measurement of textural parameters such as particle size, shape and orientation. Two basic program approaches are being developed to extend our capability beyond the measurements of dispersed particles. A preliminary paper has been published that sets out our general approach to recording and processing of SEM images (see reference below)

X-Ray Analysis Capability in the SEM Feasibility studies have been completed which show that one can expect to obtain suitable chemical information at the same time SEM images are being produced. X-ray count rates, even at specimen currents as low as 1×10^{-10} amp, are quite sufficient for non-dispersive X-ray detectors

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

- E W White and Rustum Roy, "Applications of the SEM to Ceramic Studies", Symposium Illinois Institute of Technology Research Institute, Chicago, April 1968.
- E W White, H A McKinstry and G G Johnson, Jr., "Computer Processing of SEM Images", Symposium Illinois Institute of Technology Research Institute, Chicago, April 1968.

PUBLICATIONS

- E W White and Rustum Roy, "Applications of the SEM to Ceramic Studies", Scanning Electron Microscopy, pp. 91-94, Proc. Symp. IITRI
- E W White, H A McKinstry and G G Johnson, Jr., "Computer Processing of SEM Images", Scanning Electron Microscopy, pp. 95-103, Proc. Symp. IITRI

3.2.12 THE COLLECTION AND CALCULATION OF X-RAY POWDER DIFFRACTIC^N DATA

PERS^ONNEL

V. Vand, Professor of Crystallography (deceased)
G. G. Johnson, Jr., Assistant Professor of Computer Science
I. C. Jahanbagloo, Research Associate
K. Keester, Graduate Assistant, Solid State Science
J. Dorrian, Graduate Assistant, Solid State Science

OTHER SPONSORSHIP

American Society for Testing and Materials [through the Joint
Committee on Powder Diffraction Standards] (2212 and
2118).

RESEARCH REPORT

The inclusion of good standard reference patterns to any retrieval file is necessary if the file is to be useful to any wide audience. The specific aim of the project is to obtain powder diffraction patterns of materials heretofore not included in the ASTM Powder Diffraction File--not correct existing questionable patterns--the goal of the NBS Fellowship project. The project is two-fold: (i) to obtain rare crystals and record their characteristic powder diffraction pattern on a AEG Guinier focusing camera and (ii) to calculate the theoretical diffraction pattern on those materials whose single crystal data has been obtained but the sample is unobtainable for powder diffraction work. Both programs are producing data specially for the ASTM File with the ultimate aim of the inclusion of the best possible data on as many different substances as possible. Most of the results of this project are being sent to ASTM for immediate inclusion in the ASTM File.

The theoretical aspect of indexing (hkl) the existing ASTM patterns will also serve two purposes. First, to assign proper unit cells to the unindexed substances in the ASTM File, and second, to "clean" the file of those patterns which contain contamination lines and whose pattern is really a mixture of two

substances. This method of approach is from a combination of theory of equations and theory of numbers and the results are quite encouraging

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

- G. G. Johnson, Jr., "New Methods of Indexing and Classifying X-Ray Powder Patterns", American Crystallographic Association Meeting, August 1967
- G. G. Johnson, Jr., "The Use of the Guinier Camera for the Identification of Organic Polycrystalline Materials", Chas. Pfizer Company, February 1968.
- G. G. Johnson, Jr., "The Indexing Problem in Powder Diffraction", Bell Laboratories, May 1968
- G. G. Johnson, Jr., "Modern Identification Techniques of X-Ray Powder Diffraction", Pennsylvania State University Colloquium, May 1968

PUBLICATIONS

- V. Vand, G. G. Johnson, Jr. and I. C. Jahanbagloo, "New Methods of Indexing and Classifying X-Ray Powder Patterns", Am. Crystallographic Assoc. Summer Mtg., p. 45 (1967).
- I. C. Jahanbagloo, V. Vand and G. G. Johnson, Jr., "Calculated X-Ray Patterns and Their Application in Quantitative Interpretations", MRL Monograph No. 3, 77 pages (1968).
- V. Vand and G. G. Johnson, Jr., "Indexing of X-Ray Powder Patterns, Part I. The Theory of the Triclinic Case", accepted. Acta Cryst. (1968).
- K. L. Keester, G. G. Johnson, Jr. and V. Vand, "X-Ray Powder Data for Tychite", submitted, Am. Mineral. (1968).

3.2.13 CORRELATION AND COMPUTERIZATION OF SINGLE CRYSTAL DATA

PERSONNEL

G. G. Johnson, Jr., Assistant Professor of Computer Science
L. B. Taylor, Graduate Assistant, Computer Science

OTHER SPONSORSHIP

National Bureau of Standards (4936-9)

RESEARCH REPORT

The forthcoming publication of the third edition of the crystallographic reference "Crystal Data" has been delayed for over a year due to problems in ascertaining the accuracy and reliability (and also sorting and handling of the linofilm paper tapes) of the data once it is keyboarded for production (using a linofilm phototypesetter). The present work at Penn State was designed to develop and write a computer program to check this data. Reports, in the form of computer printout of scanned data, are sent to the National Bureau of Standards almost weekly.

The data is checked with the programs for proper space groups and diffraction aspects, correct chemical formulae, properly reduced unit cells, correct density, correct axial ratios, and transformation matrices. The result to the National Bureau of Standards is the highest possible reliability in a reference work and also, and more importantly, a computer readable data base on magnetic tape for future publications and computer retrieval systems.

THESES, DEGREES GRANTED

L. B. Taylor, M S. in Computer Science, 1968: "Crystal Data Editor - A Study in Non-Arithmetic Programming".

PAPERS PRESENTED

- G. G. Johnson, Jr., "Computerizing of Crystal Data", American Crystallographic Meeting, August 1967.
- G. G. Johnson, Jr., "The Computerization of a Large Crystallographic Data File and its Corresponding 'Pattern Recognition Retrieval' System", Computer Science Colloquium, Pennsylvania State University, October 1967.

PUBLICATIONS

- G. G. Johnson, Jr., V. Vand and I. C. Jahanbagloo, "Computerizing of 'Crystal Data'", Am Crystallographic Assoc. Summer Meeting, p. 44 (1967).
- L. B. Taylor and G. G. Johnson, Jr., "Computerized Numeric Proofreading for a Linofilm Phototypesetter" (submitted for publication 1968).
- L. B. Taylor and G. G. Johnson, Jr., "Crystal Data Editor: Automatic Proofreader for 1968 Edition", J. Chem. Doc., June 1968.

3.2.14 THE STORAGE AND RETRIEVAL OF X-RAY DATA AND OTHER DATA BASES

PERSONNEL

V. Vand, Professor of Crystallography (deceased)
G. G. Johnson, Jr., Assistant Professor of Computer Science
L. B. Taylor, Graduate Assistant, Computer Science
R. McMillan, Graduate Assistant, Computer Science

OTHER SPONSORSHIP

American Society for Testing and Materials [through the sponsorship of the Joint Committee on Powder Diffraction Standards] (2212)

RESEARCH REPORT

The ASTM Information Processing Grant is a general project with the wide aim to accelerate the means of data storage and retrieval. One aspect of work during the year involved the production of new indices to the Powder Diffraction File using a special upper/lower case high-speed print chain specifically designed for the X-ray powder diffraction books. Another task was the conversion of the IBM Datatext (1460) System to the local IBM 360/67. This system is being considered for remote job entry of the ASTM Powder Data File by all the editors of these references.

The introduction by RCA of the Spectra 70/822 and by IBM of the 2680 led the area of photocomposition to these high speed devices. Some software development in these lines was developed and recommendations made as to feasibility. The conversion of all IBM 7074 computer programs of crystallographic interest to the IBM 360/67 was done when the IBM 7074 was removed from Penn State.

The writing of a multiphase X-ray powder diffraction identification program continued (begun in 1965) with the system being completely converted to the IBM 360. The Search System is presently used in about 80 universities, industries and government labora-

tories. This system using an IBM 360/67 and programs written in FORTRAN IV (H level) can scale the 18,000 powder patterns on the ASTM Powder Diffraction File in about 44 seconds (while solving a 7-component mixture). This search system is presently running on IBM, GE, CDC and UNIVAC second and third generation hardware. The system is in its seventh version with suggestions and criticisms being responsible for the improved versions.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

- G. G. Johnson, Jr., "An Information Retrieval System for Analytical Chemistry Using X-Ray Powder Diffraction", Computers in Chemistry, LaJolla, California, June 1967.
- G. G. Johnson, Jr., "Computerized Multiphase X-Ray Powder Diffraction Identification System", Diffraction Conference, Denver, Colorado, August 1967.
- G. G. Johnson, Jr., "Recent Changes in the Powder Diffraction File", Diffraction Conference, Pittsburgh, Pennsylvania, November 1967.
- G. G. Johnson, Jr., "A Computer 'Pattern Recognition' System for the Solution of Mineralogical Powder Patterns", Geological Society of America, November 1967.
- G. G. Johnson, Jr., "Modern Techniques in X-Ray Powder Diffraction", Industrial Coupling Program, Pennsylvania State University, November 1967.
- G. G. Johnson, Jr., "Computers as a Tool in the Characterization of Materials", National Education Television, January 1968.
- G. G. Johnson, Jr., "The Application of Computers for the Rapid Publication of Technical Journals", American Institute of Physics, February 1968.

- G. G. Johnson, Jr , "The Hardware-Software Interface in the Laboratory", American Oil Company, May 1966
- G. G. Johnson, Jr. , "Phase Identification on the GE 645", Bell Laboratories, June 1968
- G. G. Johnson, Jr. , "The 3 C's Crystallography, Computers and Chemistry", Symposium on Analytical Chemistry, Pennsylvania State University, June 1968

PUBLICATIONS

- G. G. Johnson, Jr and V Vand, "A Computerized Powder Diffraction Identification System", *Ind Engr Chem.* 59, 18 (1967)
- G. G. Johnson, Jr , V. Vand and I C Jahanbagloo, "Recent Changes on the Powder Diffraction File", Diffraction Conference Paper E-2, Pittsburgh (1967)
- G. G. Johnson, Jr and V Vand, "Computer 'Pattern Recognition' System for the Solution of Mineralogical Powder Patterns", *Geol Soc Am Spec Paper* (1967)
- G. G Johnson, Jr and V Vand, "A KWIC Guide to the Inorganic Powder Diffraction File", *ASTM Spec Pub 1S-17K*, American Society for Testing and Materials. 358 pp. (1967)
- E. W. White, H. A. McKinstry and G G Johnson, Jr. , "Computer Processing of SEM Images", Scanning Electron Microscopy/1968, Proc. of Symposium on the Scanning Electron Microscope - The Instrument and its Applications, Chicago, Illinois, p. 95-103 (1968).
- G. G. Johnson, Jr. and V. Vand, "Computerized Multiphase X-Ray Powder Diffraction Identification System", X-Ray Conference, Denver, Advances in X-Ray Analysis, Vol. 11, pp. 376-384 (1968)
- G. G. Johnson, Jr and V Vand, "FORTRAN IV Programs (Version 7) for the Identification of Multiphase Unknown Powder Diffraction Patterns Using the Joint Committee's Powder Diffraction File", (accepted, ASTM 1968)

- G. G. Johnson, Jr. and V. Vand, "A KWIC Guide to the Powder Diffraction File", (Accepted, ASTM 1968).
- G. G. Johnson, Jr. and L. B. Taylor, "Simplified File Management Utilizing IBM Datatext", (Submitted for publication, IBM 1968).

3.3

PROPERTIES OF MATERIALS

The principal goal of materials science is to relate the composition and structure of any solid to its properties. The progress of the field is, in fact, measured by the degree to which this relationship can be refined. The previous sections have described our efforts in the first two phases of preparing and characterizing materials; this section will deal with phenomenological and theoretical studies of the physical properties of the material. Ideally, all materials on which physical measurements are made should have been prepared and characterized in our laboratories before reaching those making the measurements. In practice, the extent of such interaction between the chemical groups (preparers and characterizers) and the physical property groups is measured by the extent to which such a flow of materials takes place. A laboratory where considerable innovative synthesis and growth research takes place should confer a special advantage on those interested in measurements since they have first access to new phases. Again, in practice, we are encouraged by the extent to which this has happened although it is obviously a small part of the total. Thus, results of research in this area are grouped broadly by the property measured, with the exception of the work on one material category--carbon.

3.3.1 MECHANICAL AND ELASTIC PROPERTIES

This section contains a summary of several experimental and theoretical research projects that range from macroscopic elastic properties (second and higher order elastic constants) and mechanical strength to lattice theoretical calculations of anharmonic material properties, point defects, solid solutions and free surfaces of ionic crystals.

3.3.1.1 NONLINEAR ELASTIC PROPERTIES

PERSONNEL

G. R. Barsch, Associate Professor of Solid State Science
Z. P. Chang, Research Associate, Solid State Science
J. H. Gieske, Graduate Assistant, Physics
E. K. Graham, Graduate Assistant, Geophysics
D. C. Miller, Graduate Assistant, Solid State Science
H. E. Shull, Graduate Assistant, Engineering Mechanics
R. Srinivasan, Senior Research Associate, Solid State Science
E. Jones, Technician

OTHER SPONSORSHIP

Atomic Energy Commission (AT(30-1)-2581)
Office of Naval Research (656(27))
University (funds from Space Science and Engineering Laboratory
and Ordnance Research Laboratory)

RESEARCH REPORT

Third Order Elastic Constants of Aluminum Oxide The dependence of the ultrasonic wave velocities on hydrostatic and uniaxial compression has been measured for various directions of propagation and polarization in single crystalline aluminum oxide by means of the pulse super-position method. From these results the first pressure derivatives of the six second order elastic constants and the complete set of the fourteen third order elastic constants have been determined. The results were found to agree approximately with theoretical data for the hexagonal close packed structure with central forces between nearest neighbors. This indicates that the elastic constants of aluminum oxide and their pressure dependence are essentially determined by the hexagonal close packed framework of the oxygen ions, with the small aluminum cations giving rise to a small correction only. The results have been used and will be used for the calculation of several anharmonic materials properties.

Pressure Dependence of the Elastic Constants of Alkali Halides.

The dependence of the second order elastic constants on hydrostatic pressure has been measured ultrasonically for several alkali halide single crystals up to 10 Kb at room temperature, and for CsI as a function of temperature between room temperature and 300°C. The sensitivity of the ultrasonic interferometer used was large enough to measure the second pressure derivatives of the elastic constants in addition to the first pressure derivatives. From the first pressure derivatives linear combinations of the third order elastic constants, and from the second pressure derivatives linear combinations of the fourth order elastic constants have been determined. The results are being analyzed in terms of lattice theoretical models based on Coulomb and Born-Mayer type interaction and include the effect of thermal motion in the quasiharmonic approximation. Application has been and is being made to the calculation of anharmonic material properties. In addition the ultrasonic equation of state for CsI has been proposed as basis for using CsI as a pressure gauge in a high pressure X-ray camera up to several hundred kilobars.

Pressure Dependence of the Elastic Constants of Olivine The dependence of the isotropic elastic constants of polycrystalline (hot-pressed) olivine on pressure and temperature was measured ultrasonically up to 10 Kb and 450°C. In addition, the nine elastic constants of single crystalline olivine are being measured as a function of pressure and temperature for pure synthetic crystals grown by the flame fusion method. The results will be used to interpret seismic velocity data in terms of composition versus depth profiles in the earth.

Third Order Elastic Constants of Polycrystals The approximations by Voigt, Reuss and Hill for calculating the elastic constants of polycrystals from the elastic constants of single crystals were extended to the third order elastic constants and used to calculate the polycrystalline third order elastic constants for all materials for which the single crystal data are available.

In addition, the anisotropy of the third order elastic constants is discussed. It was found that for all materials considered the anisotropy of the third order elastic constants is much larger than that of the second order elastic constants and that a weak correlation exists between the anisotropy of the third order elastic constants and that of the second order elastic constants. Measurements of the isotropic third order elastic constants were

made for polycrystalline magnesium oxide and aluminum oxide. In magnesium oxide an analysis of the data showed strong effects of strain aging. For aluminum oxide the experimental data agreed well with the theoretical data obtained from the single crystal constants by means of the Voigt-Reuss-Hill average method.

Anharmonic Materials Properties The experimental data of the third order elastic constants were used to investigate theoretically the thermal equation of state in the quasi-harmonic approximation in the elastic continuum limit. For cesium halides the temperature dependence of the bulk modulus, the Grueneisen parameter and its pressure dependence can be accounted for satisfactorily in this manner. For aluminum oxide the two Grueneisen parameters parallel and perpendicular to the trigonal axis that are calculated from the third order elastic constants agree with the experimental data in the high temperature limit (above room temperature) when calculated from thermal expansion measurements.

Elastic Constants of Complex Phases Chung and Buessem report that the previously measured elastic constants of such hexagonal crystals as apatite, beryl, and several metals do not fit the general elastic anisotropy curves. In order to clarify these deviations from the anisotropy curves for apatite and beryl which contain less plastic strains compared with metals, the second-order elastic constants of apatite were re-measured, using the ultrasonic pulse superposition method.

THESES, DEGREES GRANTED

J. H. Gieske, Ph.D. in Physics, 1968. "The Third Order Elastic Coefficients and Some Anharmonic Properties of Aluminum Oxide"

PAPERS PRESENTED

None

PUBLICATIONS

G. R. Barsch and Z. P. Chang, "Effective Second and Higher Order Elastic Constants of Cubic Crystals Under Hydrostatic Pressure" J. Appl. Phys. 39, 276 (1968)

- G. R. Barsch. "Relation Between Third Order Elastic Constants of Single Crystals and of Polycrystals. J Appl Phys. 39 (1968) (in press)
- Z. P. Chang, G. R. Barsch and D. L. Miller, "Pressure Dependence of Elastic Constants of Cesium Halides", Phys Stat Sol 23, 577 (1967)
- Z. P. Chang and G. R. Barsch, "Nonlinear Pressure Dependence of Elastic Constants and Fourth Order Elastic Constants of Cesium Halides". Phys Rev Let 19, 1381 (1967)
- Z. P. Chang. "Pure Transverse Modes of Elastic Waves in Crystals". J Appl Phys 39 (1968) (in press)
- J. H. Gieske and G. R. Barsch. "Pressure Dependence of the Elastic Constants of Single Crystalline Aluminum Oxide", Phys Stat Sol 29 (1968) (in press)
- R. Srinivasan. "Lattice Theory of Third Order Elastic Constants of Germanium and Silicon" J Phys Chem Sol 28, 2385 (1967)
- R. Srinivasan, "Lattice Theory of the Elastic Dielectric", Phys. Rev 165, 1041 (1967)
- R. Srinivasan, "Lattice Theory of the Elastic Dielectric Application to the Fluorite Lattice". Phys Rev 165, 1054 (1967)

3.3.1 2

THEORETICAL STRENGTH FOR
BRITTLE FRACTURE

PERSONNEL

G R Barsch, Associate Professor of Solid State Science
R C Hollinger, Graduate Assistant Solid State Science
J H Gieske Graduate Assistant, Physics
J Schiff, Computer Programmer

OTHER SPONSORSHIP

Office of Naval Research (Nour (656-27))
University Support (Naval Ordnance Systems Command)

RESEARCH REPORT

Orientation Dependence of the Theoretical Strength of Aluminum Oxide The theoretical strength of aluminum oxide was calculated from a previously developed theory on the elastic stability limit of initially stressed crystals by using the measured values of the second and third order elastic constants. The calculations were made for four different crystallographic planes and indicate a weak orientational dependence of the theoretical strength. The theoretical results are about two times larger than experimental tensile strength data obtained from whiskers.

Theoretical Strength of Alkali Halide Crystals The purpose of this project is to investigate the convergence of the Taylor expansion of the strain energy with respect to the strain components for large deformations and to determine the order of the approximation which is required in order to obtain accurate values of the theoretical strength and its dependence on orientation. To this end the elastic constants of NaCl and KCl have been calculated up to sixth order from a central force potential consisting of Coulomb, van der Waals and Born-Mayer-type repulsive interaction. With these data the elastic stability limit is being determined for various load conditions and in various approximations. This work is still in progress.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

None

PUBLICATIONS

None

3.3.1.3

THEORY OF IONIC CRYSTALS

PERSONNEL

G. R. Barsch, Associate Professor of Solid State Science
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B. N. Achar, Graduate Assistant, Solid State Science

OTHER SPONSORSHIP

National Science Foundation (GP 3232)
University Funds (Graduate School Fellowship)

RESEARCH REPORT

Quantum Theory of Interatomic Forces in Ionic Crystals. The effect of quantum mechanical many body forces on the elastic constants of ionic crystals has been investigated by using the approach developed by Löwdin. In this method the occurrence of three-body forces of central type is accounted for by means of exchange and overlap terms arising from orthogonalized atomic orbitals. The elastic constants and their dependence on hydrostatic pressure were calculated for LiF, NaF, and MgO from this approach which was extended so as to include second nearest neighbor anion-anion interactions. Satisfactory agreement with the observed deviations of the elastic constants from the Cauchy relations is found.

Lattice Dynamics of Surfaces of Ionic Crystals. The equilibrium configuration and the occurrence of surface modes of vibration in a semi-infinite crystal have been studied on the basis of the point ion model. The displacements and the energy due to the relaxations occurring if the ions in a semi-infinite crystal are allowed to move from the positions which they occupy in an infinite crystal are comparable, but somewhat larger than the theoretical values calculated by Benson by a different approach and by including electronic polarizability and van der Waals interaction. The surface modes were obtained by means of the scattering matrix. For a (100) surface of NaCl longitudinal and transverse optical modes occur which lie very close to the longi-

tudinal and transverse optical frequencies of the infinite crystal for infinite wavelength. In addition, longitudinal and transverse acoustic modes are found that reduce in the long wavelength limit to Raleigh waves

Lattice Theory of the Heats of Formation of Alkali Halide Solid Solutions. The composition dependence of the heat of formation of alkali halide solid solutions over the entire composition range has been calculated from the substitutional defect model of Dick and Das and the assumption of Vegard's law on an atomistic scale. Good overall agreement with the experimental data that are available for eight binary systems is found.

THESES, DEGREES GRANTED

D. L. Fancher, Ph D in Solid State Science, 1968. "Lattice Theory of Alkali Halide Solid Solutions"

PAPERS PRESENTED

None

PUBLICATIONS

S. Y. La and G. R. Barsch, "Pressure Derivatives of Second-Order Elastic Constants of MgO", Phys. Rev 172, 357 (1968).

3.3.1 4 MATERIAL INSTABILITY AT HIGH PRESSURE

PERSONNEL

G. R. Barsch, Associate Professor of Solid State Science
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D. L. Fancher, Graduate Assistant, Solid State Science

OTHER SPONSORSHIP

National Science Foundation (GK 1686X)
National Science Foundation Traineeship

RESEARCH REPORT

Lattice Theory of Solid Solubility of Alkali Halide Solid Solutions. Previous calculations on the composition dependence of the heat of formation of alkali halide solid solutions based on the substitutional defect model of Dick and Das were extended to the calculation of solid solubility of the chemical spinodal and of the coherent spinodal, both at zero pressure, and as a function of pressure. Comparison with experimental data at zero pressure indicates that the entropy of mixing shows large deviations from ideal mixing. This effect could be taken into account only for the system KCl-KBr for which experimental data on the composition dependence of the elastic constants are available. To overcome this deficiency theoretical calculations on the composition dependence of the bulk modulus have been started on the basis of the modified model of Dick and Das mentioned above.

Pressure Dependence of Phonon Dispersion Curves. Lattice theoretical calculations on the pressure dependence of the phonon dispersion curves in alkali halides have been started in order to investigate the occurrence of mode instabilities and the mechanism of the phase transition from the rocksalt to the cesium chloride structure. This work is still in progress.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

None

PUBLICATIONS

None

3.3.1 5 MECHANICAL PROPERTIES OF MICA

PERSONNEL

K. Vedam, Associate Professor of Solid State Science
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OTHER SPONSORSHIP

Army Materials and Mechanics Research Center (DA-19-0660
AMC-325(X))

RESEARCH REPORT

Tensile and bending experiments on micas reveal nonlinear stress-strain behavior in micas indicating slippage between the layers. Interpretation of the Berg-Barrett pattern of muscovite mica along with the results obtained with rocking curve studies, condensation of water droplets on freshly cleaved mica surfaces, and the Lang technique, indicate that the layer structure of muscovite is not truly planar but appears to be corrugated somewhat similar to the layers in antigorite. Because of the corrugations, mica is noticeably anisotropic even within the layers; the sheets are more easily bent parallel to the corrugations.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

K. Vedam, R. E. Newnham, J. W. McCauley, J. Caslavsky and R. Roy, "Relationship of the Mechanical Properties to the Structure of Micas", Structural Ceramics Seminar, IITRI, Chicago, March 1968

PUBLICATIONS

- K. Vedam, R. E. Newnham, J. McCauley, J. Caslavsky and R. Roy, "Relation of the Mechanical Properties to the Structure of Ionic Solids", Proc. of Second Symposium on Structural Ceramics, Gordon & Breach Science Publishers, Inc. (1968) (in press)

3.3.2

MAGNETIC PROPERTIES

PERSONNEL

L. N. Mulay, Professor of Solid State Science
J. T. Dehn, Research Associate, Solid State Science
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W. J. Danley, Jr., Graduate Student, Solid State Science
F. J. Trexler, Graduate Student, Solid State Science
H. G. Ziegenfuss, Graduate Student, Solid State Science
N. L. Hofmann, Graduate Student, Chemistry

OTHER SPONSORSHIP

Atomic Energy Commission (At(30-1)-2581)
Armstrong Cork Company (Polymer Grant, Research Project)
Paint Research Institute (Grant-in-Aid)
National Science Foundation (GP-3232)

RESEARCH REPORTS

Magnetic Studies on High Temperature Oxides of Titanium.

These oxides or ionic phases exhibit interesting properties including semiconduction and transitions from semi to metallic conduction at certain temperatures. This work was undertaken to elucidate these transitions and structures in these phases. The magnetic susceptibilities of a number of oxides, such as Ti_2O_3 , Ti_3O_5 , Ti_4O_7 , Ti_5O_9 , Ti_6O_{11} , Ti_7O_{13} , Ti_8O_{15} , Ti_9O_{17} and $Ti_{10}O_{19}$, and TiO_2 have been studied as a function of temperature. The antiferromagnetism of Ti_4O_7 , Ti_5O_9 , Ti_6O_{11} has been investigated in detail and explained on the basis of variation of stoichiometry and the available data on crystal structures. The semiconductor to metal transitions observed respectively in Ti_2O_3 and Ti_3O_5 have been interpreted in terms of noncooperative and cooperative effects. Other phases were found to show an apparent paramagnetic effect, and to deviate from the Curie Weiss law; TiO_2 itself showed a temperature independent magnetic susceptibility. The results have been correlated with some optical absorption and Hall effect studies which show evi-

dence of free carriers in certain cases. The effective electronic mass in Ti_2O_3 and Ti_3O_5 have been computed on the basis of the Fermi-Peirls equation and the assumptions associated with the equation.

Magnetic measurements on polycrystalline samples are being extended to liquid helium temperatures, and will be used in the elucidation of the energy band gap picture in these phases.

Superparamagnetism of Iron Dispersions in Silicate Matrices, Magnetic and Mossbauer Studies This work was undertaken to study at a fundamental level the transitions from para to superpara to ferromagnetic behavior of iron. For this purpose novel syntheses were undertaken to disperse iron and to control the size of clusters of iron "atoms" or "ions" in (i) the vitreous silicate matrix and (ii) in the molecular sieve type zeolite matrix. In the first case Fe^{2+} and Fe^{3+} ions, introduced in the silicate matrix were reduced by carbon monoxide (CO) and the cluster sizes were controlled by the total concentration of iron introduced and subsequent "annealing" procedures. In the second case several "covalent" compounds of iron were introduced in the zeolite matrix and allowed to oxidize. Several experimental parameters were controlled to obtain varying cluster sizes. In all cases transitions from the "magnetically dilute" paramagnetic to sub-domain superparamagnetism were observed. In the zeolite system the clusters could be converted to the ferromagnetic domain dimensions.

Several parameters such as the cluster size, moment, number of particles per cluster, etc., were obtained from the magnetic data. The overall nature of gradual transitions from para to ferromagnetism were confirmed by Mossbauer studies. These studies in turn are being used to study electronic relaxation of iron clusters under varying conditions.

Mixed Magnetic Ordering in Coordination Complexes of Transition Metals; Magnetic and Mossbauer Studies A number of dimeric and polymeric coordination complexes of transition metals, and especially of iron, have been investigated, with a view to understand the nature of the metal-metal bond in terms of the Heisenberg exchange interaction "J" between unpaired electronic spins on neighboring metal atoms, crystal field effects of the organic or inorganic ligands. Several complexes exhibit "antiferromagnetism", which seems to arise from "intramolecular" antiferro-

magnetism (short range ordering between metal atoms isolated within the ligands) and a long range ordering arising from coupling of cations through anions. Quantitative study of the exchange interaction, which seems to vary from $J = -100$ to -300 cm^{-1} have been made. Mossbauer spectroscopy has been used to identify the valence state, and in general to unravel the electronic structures and transitions in coordination complexes and "salts" such as Fe_2TeO_6 .

Molecular Orbital Descriptions. Magnetic Anisotropy and Mossbauer Studies on Metallocenes. This work was undertaken to put "qualitative" concepts of organic and organometallic chemistry on a "quantitative" basis and to use the approaches of solid state chemistry to understand submolecular and electronic structure in metallocenes, which are structurally fascinating and technologically promising in many ways.

The " π electron densities" (arising from the p wave functions of carbon atoms and the diamagnetic ring currents) in the cyclopentadienyl rings (C_5H_5 or Cp) in Ferrocene Cp_2Fe , Ruthenocene Cp_2Ru and Osmocene Cp_2Os , were obtained through rather difficult and elaborate measurements of magnetic susceptibility anisotropy on single crystals of these compounds.

The π electron densities obtained per Cp ring in Ferrocene (4.6), Ruthenocene (3.1) and Osmocene (2.8) beautifully explain the decrease in electrophilic reactivity in this series observed by organic chemists and the high resolution (proton magnetic resonance) chemical shifts, etc.

The anisotropy studies, further help support one particular M O theory (Dahl and Bahlhausens) applied to Ferrocene in preference to that proposed by Schustrovich and Dyatkina, suggesting that magnetic anisotropy provides a sensitive criterion for testing combination of atomic wave functions. The M O theories have been extended to ruthenocene and osmocene, and the π -electron densities derived therefrom show good agreement with the experimental values.

Mossbauer measurements on single crystals of ferrocene have also proved helpful in understanding the electronic structure of ferrocene; however, the magnetic anisotropy measurements have been far more successful.

Magnetic and E P R Studies on Free Radical Activity in Normal and Cancer Tissues A study of magnetic susceptibility and electron paramagnetic resonance spectra of melanoma (melanotic and amelanotic) and normal tissues from mice showed significant differences in line shapes, and intensities. The intensities and values have been successfully correlated with trace metal analysis and known biochemical reactions. The free radical activity and the concentration of Cu^{2+} and Fe^{3+} was generally higher in the melanotic (S-91) tumor than in the amelanotic tumor. Other tissues such as liver, spleen, heart, kidney, brain etc showed varying amounts of free radical activity, but considerably less than in the cancerous tissues and did not reveal E P R signals attributable to paramagnetic ions. These findings suggest that free radical activity in melanoma (S-91) may be attributed partly to melanin and intermediates of various enzymatic reactions. Similar biomedical information has been obtained in other cases.

Proton Magnetic Resonance Studies on Polymers Broad line N M R has been used to characterize polystyrene of "controlled" molecular weight (monodispersed samples) and of polyvinyl chloride polymers of widely varying molecular weight. The technique is found to be excellent for (i) defining the relative "amorphous" and "crystalline" phases in these polymers, (ii) for obtaining activation energies for reorientation processes of the polymer chains, (iii) for differentiating between some of these motions ("oscillation", "wagging", "crankshaft motion", etc) and (iv) for studying thermal degradation.

An allied study on the plasticizer-P V C polymer interaction has proved to be significant both at the fundamental and technological levels. The studies are being extended to elucidate the kinetics of radiation damage in several polymers.

THESES. DEGREES GRANTED

- D W Collins, Ph D in Solid State Science, 1968. "Superparamagnetism of Iron Dispersions in Silicate Matrices"
- C P Chen M S in Mechanical Engineering, 1968. "Effect of Electric and Magnetic Fields on Chemical Reactions"
- V W Withstandley, D Ed in Physics, 1968. "Magnetic Susceptibility Anisotropy Studies on Ruthenocene and Osmocene"

- L. K. Keys, Jr., Ph D in Solid State Science, 1966. "Magnetic Susceptibility and Resonance Studies on Adsorbed Oxygen. Formation of O_4 Species "

PAPERS PRESENTED

- L. N. Mulay, "Magnetic and Mossbauer Studies on Iron Dispersions in Molecular Sieves (Zeolites)", Eighth International Conference on Magnetism and Magnetic Materials (IEEE), Washington D C, April 1968
- L. N. Mulay, "Magnetic and Mossbauer Studies on Iron Dispersions in Silicate Matrices", Physics Chemistry Division, 155th Meeting, American Chemical Society, San Francisco, April 1968
- L. N. Mulay, "Magnetism and the Metal-Semiconductor Transition in Ti_3O_5 ", American Physics Society Meeting Washington, D C, April 1967
- L. N. Mulay, "Exchange Interaction Between Magnetism and Mossbauer Spectroscopy", Third Mossbauer Symposium, New York, New York. January 1967
- L. N. Mulay, "Magnetic Susceptibility Studies on Physical Adsorption of Paramagnetic Gases", Symposium. Division of Colloid and Surface Chemistry, American Chemical Society 153rd Meeting, Miami, Florida, April 1967
- L. N. Mulay, "Basic Concepts of Mossbauer Spectroscopy, Exciting Aspects of Organometals Magnetochemistry and Whatnot", Symposium on Mossbauer Spectroscopy, Central Regional Meeting. American Chemical Society Akron, Ohio, May 1968
- L. N. Mulay, "Characterization of Controlled Molecular Weight Polymers by Nuclear Magnetic Resonance" Symposium on Polymers, Middle Atlantic Regional Meeting of the American Chemical Society. Philadelphia. February 1968

PUBLICATIONS

- I L Mulay and L N Mulay, "Magnetic Susceptibility and E S. R. Absorption Spectra of S-91 and S-91 A Mouse Melanomas", J Nat Cancer Inst 39, 735 (1967)
- I L Mulay, R L McCarl, J Nuss and L N Mulay, "Copper and Free Radical Accumulation in Liver of Calves with Inherited Hydrocephalus". Am J Vet Res 28, 1909 (1967)
- L N Mulay, Magnetic Susceptibility A Monograph 132 pp, John Wiley & Sons New York, New York (1967)
- L N Mulay, "Philosophy of Research. New Projects in Mossbauer Spectroscopy of Systems with Weak Magnetic Interactions", Mossbauer Methodology, Vol III, pp 79-102 I. J Gruverman, Ed. Plenum Press, New York (1967)
- L N Mulay and F D Trexler, "Characterization of Polystyrenes of Controlled Molecular Weight by Nuclear Magnetic Resonance Spectroscopy" Mat Res Bull 2, 781 (1967)
- L N Mulay and D W Collins "Super Paramagnetism of Iron Dispersions Within a Silicate Matrix. Magnetic Susceptibility and Mossbauer Studies". Japan J Appl Phys 6, 1342 (1967)
- L N Mulay and I L Mulay, "Magnetic Susceptibility. Recent Aspects of Instrumentation and Applications to Chemistry and Solid State Science" Analyt Chem 40, 440R (1968)
- L N Mulay, D W Collins and J T Dehn, "Superparamagnetism and Mossbauer Spectroscopy A Review and New Results of Iron Dispersions". Mossbauer Methodology Vol III, pp. 103-122 I. J Gruverman Ed. Plenum Press, New York (1967)
- L N. Mulay, D Deb-Ray and E Ryba, "Magnetic Susceptibilities of Some Rare Earth-Zinc (R Zn₂) Intermetallic Compounds", J. Appl Phys 38 3459 (1967)

3.3.3

ELECTRICAL PROPERTIES

Work in ferroelectric and dielectric studies, as part of a broad program of research in electrical properties, has been the means of attracting special attention to the laboratory. This is indicated by the award received by two members of the faculty from the Electronics Division of the American Ceramic Society for the best paper published in the journal or bulletin in the previous ten-year period

3.3.3.1 FERROELECTRIC AND ELECTRO-OPTIC STUDIES

PERSONNEL

L E Cross, Professor of Electrical Engineering
 J Fousek, Senior Research Associate (Visiting)
 A Fouskova, Research Associate (Visiting)
 M A Saifi, Graduate Student, Electrical Engineering
 J Dougherty, Graduate Student, Electrical Engineering
 K Seely, Graduate Student, Electrical Engineering
 R C Pohanka, Graduate Student, Solid State Science
 D Payne, Graduate Student, Solid State Science
 J W. Smith, Graduate Student, Solid State Science

OTHER SPONSORSHIP

Air Force Avionics Research Laboratory (F33615-67-C-1427)

RESEARCH REPORT

Bismuth Titanate ($\text{Bi}_4\text{T}_{13}\text{O}_{12}$) Working in very close cooperation with Mr S E Cummins and his group at Avionics Laboratory, a detailed study has been made of the optical, dielectric, domain and symmetry properties of bismuth titanate. The low monoclinic symmetry is shown to give unique switchable optical properties, the indicatrix tilting through 45° on reversal of the polarization P_z along the 'c' axis. Using the methods of Aizu and Fousek the phenomenology of the point group $4/\text{mmm}$, the prototype for bismuth titanate has been developed in detail to explain the observed optical dielectric and static domain properties.

Lithium Thallium Tartrate Lithium thallium tartrate is a ferroelectric with Curie temperature at 12°K . Measurements of the dielectric properties show the absence of a Curie peak in the original data of Matthias was due to the high measuring field used. Very low field measurements show a normal Curie-Weiss behavior, with a strong peak in ϵ at T_c . Behavior under bias fields, and the 'hysteresis loops' below T_c show several unusual features in the domain behavior at such low temperatures.

Domain Studies in Ferroelectric Crystals In collaboration with Dr V Janovec, a new general treatment of domain walls has been developed, which makes it possible to predict all possible domain walls in all species of ferroelectrics, for perfect infinite crystals. Based on this theory, new types of "non-crystallographic" walls are predicted. These strange walls (S-walls) are shown to agree closely with some of the heretofore inexplicable features of the domain structure in nickel iodine boracite.

Strontium Titanate Low temperature studies have been made of very carefully annealed single crystals of SrTiO_3 . These crystals show a most unusual double hysteresis at temperatures below 50°K which may be explained as a switching between an anti-ferroelectric and a field forced paraelectric state. The behavior can be analyzed quantitatively in terms of a simple Kittel free energy function.

Electrostriction in BaTiO_3 Using the high pressure data of Samara on the dielectric properties of BaTiO_3 crystals, it has been shown that the change of the Curie-Weiss slope of the dielectric constant in the paraelectric phase, as a function of pressure, may be attributed to a very weak temperature dependence of the electrostriction constant ($Q_{11} + 2Q_{12}$).

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

None

PUBLICATIONS

- S E Cummins and L E Cross, "Crystal Symmetry, Optical Properties and Ferroelectric Polarization of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Single Crystals", Appl Phys Let 10, 14 (1967)
- S E Cummins and L E Cross, "Electrical and Optical Properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Single Crystals, J Appl. Phys 39, 2268 (1968)

- L. E. Cross and R. C. Pohanka, "A Thermodynamic Analysis of Ferroelectricity in Bismuth Titanate". J Appl Phys 39 (1966) (in press)
- J. Fousek and F. Janovec, "Orientations of Domain Walls in Ferroelectrics", Bull Am Phys Soc 12, 902 (1967).
- L. E. Cross and M. A. Saifi, "Electric Double Hysteresis in Annealed Single Crystals", Phys Let. (1968) (in press)
- A. K. Goswami and L. E. Cross, "On the Pressure and Temperature Dependence of the Dielectric Properties of the Perovskite Barium Titanate", Phys Rev (1968) (in press)

3 3 3 2 DIELECTRIC AND STRUCTURAL STUDIES

PERSONNEL

L E Cross Professor of Electrical Engineering
 B Krause, Senior Research Associate
 C F Groner Graduate Student, Solid State Science
 J. W. Smith, Graduate Student, Solid State Science
 R. Kunz, Graduate Student, Solid State Science
 D Johnson, Graduate Student, Ceramic Science

OTHER SPONSORSHIP

Atomic Energy Commission (AT(30-1)-2581)

RESEARCH REPORT

Lead Magnesium Niobate (Dielectric Studies) Dielectric, pyroelectric, electro-optic and mechanical property studies confirm the relaxor behavior reported by Smolenskii et al., and the ferroelectric properties at low temperature. The behavior has been analyzed in terms of a lamellar heterogeneity, with submicroscopic regions of differing Curie temperature within the crystal.

Lead Magnesium Niobate (Structural Studies) Using electron diffraction and transmission microscopy the presence of an ordering (of the Mg and Nb on the "B" site of the perovskite lattice) has been demonstrated. The diffraction data are consistent with three possible superstructures, and the super cells for these have been enumerated. The range of the superlattice domains is short, and the ordering cannot be seen by X-rays. This work provides the first definitive evidence of the submicroscopic heterogeneity which is required to explain the dielectric behavior.

SrTiO₃ Crystals Containing Rare Earth Ions Dielectric relaxation is known to occur in SrTiO₃ ceramics containing bismuth titanate, or lanthanum titanate. A detailed study has now been completed of the dielectric properties of SrTiO₃ ceramics containing praeosodymium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. In

all cases dielectric relaxation was observed and the time-temperature dependence is generally similar. The sequence is discussed on the model of Skanavi which provides the most likely explanation for the observed phenomena.

Dielectric Studies of Calcium Fluoride Weak dielectric relaxation at KHz frequencies is observed in CaF_2 single crystals and ceramics doped with Nd^{3+} . Detailed analysis of the data on samples of a wide range of thickness show that the relaxation is not a surface controlled Maxwell-Wagner phenomenon. The very low $\tau_0 \sim 10^{-16}$ sec in the Arrhenius relation describing the relaxation makes it unlikely, however, that the relaxation is of dipolar defects and a model is proposed which requires a volume distribution of higher conductivity inclusions. Possible origins for such inclusions are discussed.

Dielectric Properties of Flux Grown Rutile (TiO_2) Crystals To test the efficacy of the rotating field non-contact method for measuring crystals of high permittivity, measurements have been made on very small ($v \sim 10^{-5}$ cc) crystals of TiO_2 grown by a flux method.

From the 'false dispersion' evident in the data it is possible to derive the depolarizing factor, conductivity and permittivity. The data show $\epsilon_c \sim 165$, $\rho \sim 10^6$ ohm/cm in good agreement with values for reoxidized flame fusion grown crystals. The non-contact method shows considerable promise as a technique for measuring whiskers and fibers.

Electrostriction in Alkali Halide Crystals Work has been initiated to measure the separated components of the electrostriction tensor in alkali halide crystals from the stress dependence of the dielectric permittivity. From hydrostatic measurements, $Q_{11} + 2Q_{12}$ have been measured for NaCl, NaBr, KCl, KBr. Using a special jig measurements are now being made under uniaxial stress to separate the Q_{ij} constants. The dielectric method has the great advantage that measurements are carried out under the condition $E \rightarrow 0$ so that Maxwell stresses are not induced.

THESES, DECREES GRANTED

J. W. Smith, Ph.D. in Solid State Science, 1967: "Dielectric Properties of Lead Magnesium Niobate"

PAPERS PRESENTED

None

PUBLICATIONS

- B. Krause and D. L. Gibbon. "Ordering of Mg and Nb in the Octahedral Positions of the 'Cubic' Perovskite Structure of $\text{Pb}_3\text{MgNb}_2\text{O}_9$ ", J Appl Phys (1968) (in press)
- D. W. Johnson, F. A. Hummel and L. E. Cross, "Dielectric Relaxation in Rare Earth Doped Strontium Titanate", Bull. Am Ceram. Soc. 47, 355 (1968).

3 3 3 3 ELECTRONIC PROCESSES IN SOLIDS

PERSONNEL

H K Hensch, Professor of Applied Physics
 J E Caffyn, Senior Research Associate
 W Bose, Research Associate
 M Engineer, Research Associate
 J McCormick, Graduate Assistant, Solid State Science
 W Schneider, Graduate Assistant, Solid State Science
 S Lee, Graduate Assistant, Solid State Science
 G Fabel, Research Fellow, Solid State Science

OTHER SPONSORSHIP

Atomic Energy Commission (AT(30-1)-3409)
 National Science Foundation (GP-3232)
 Army Mobility Equipment Research and Development Center
 (DA-44-009-AMC-581 (T))
 Selenium-Tellurium Development Corporation (Grant-in-Aid)

RESEARCH REPORT

The Role of Trapping Processes in Radiation Dosimetry The general aim of the work on trapping processes is to develop non-luminescence methods for radiation dosimetry. Recent experiments have been concerned with the utilization of pyroelectric materials (e.g. ZnS and natural tourmaline) for this purpose. The specimen is heated to produce a pyroelectric emf which diminishes after reaching a maximum, as a result of free carrier production. This diminution sets in earlier if the specimens have been pre-irradiated to fill shallow traps and the resulting temperature-voltage characteristic can be used as a dosimetric criterion. At the same time, the experiments throw new light upon the energetic position and properties of carrier traps.

Contact Properties of Silver Iodide Single crystals of AgI have become available as a result of the experiments (described elsewhere in this report) on crystal growth in gels. They are interesting from two points of view: (i) as substrates for experiments

on the mechanism of cloud seeding, and (ii) as ionic semiconductors. The latter properties are now being explored. The ionic conductivity at room temperature is low, with corresponding measurement complications. Special attention is being paid to the contacts as a counterpart of the work already performed under this contract on electronic semiconductors.

Electron-Photon Interaction Phenomena The current work deals with the preparation and properties of Ge-GaAs heterojunctions, with photocapacitive effects at Ge (or Si) -Collodion-Gold contacts, with photodielectric measurements on antimony iodo-sulfide and with space-charge-controlled conduction processes in CdS. It represents a general attempt to explore new, unorthodox or neglected methods of light detection.

Properties of Selenium Current-glow measurements on microcrystalline trigonal selenium have revealed structural features which may be of value for characterization purposes. In particular, two discrete trapping levels have been detected.

THESES DEGREES GRANTED

None

PAPERS PRESENTED

H. K. Henisch, "Contact Properties of Semiconductors", Solid State Physics Seminar, University of Kentucky, March 1968.

PUBLICATIONS

J. M. Toole, H. K. Henisch and K. Miyashita, "Thermovoltic Radiation Dosimetry", *Nature* 213, 698 (1967).

S. Lee and H. K. Henisch, "Photocapacitive Effect at Silicon Collodion-Gold Contacts", *J. Solid State Electronics* 11, 301 (1968).

D. N. Bose and H. K. Henisch, "Radiation Dosimetry by Current Glow in Diamond", *J. Solid State Electronics* 11, 273 (1967).

H. K. Henisch and M. H. Engineer, "Thermally Stimulated Currents in Trigonal Selenium", Physics Letters 26A, 188 (1968)

J. M. Toole and H. K. Henisch, "Pyroelectric UV Radiation Dosimetry", J. Solid State Electronics 11, (1968) (in press)

3 3 4

OPTICAL PROPERTIES OF SOLIDS UNDER PRESSURE

PERSONNEL

K Vedam, Associate Professor of Solid State Science
 F Lukes, Visiting Research Associate in Solid State Science
 T Davis, Graduate Student, Solid State Science
 D Felentzer, Graduate Student, Physics
 J L Kirk, Graduate Student, Solid State Science
 E D D Schmidt, Graduate Student, Solid State Science

OTHER SPONSORSHIP

National Science Foundation (GK-1686X)
 Selenium-Tellurium Development Association (Grant-in-Aid)

RESEARCH REPORT

Variation of Refractive Index of Solids with Pressure. This project has continued to yield interesting and exciting results on the variation of the refractive index of solids with pressure to 7 kbars. The nonlinear piezo-optic behavior observed in most solids is the manifestation of nonlinear stress-strain relationship. However, in some materials like α and β -ZnS, CdS, etc., the relationship between the change in refractive index and Lagrangian strain is nonlinear even for moderate stresses and strains, due to the proximity of the absorption edge to the radiation used in these studies.

Variation of the Optical Rotatory Power of Crystals with Pressure. The optical rotatory power of α -quartz is found to decrease linearly with uniaxial pressure along the optic axis in the visible region of the spectrum. By comparing with similar data on $d\rho/dP$ under hydrostatic conditions it is concluded that Chandrasekhar's coupled oscillator theory of optical activity of α -quartz is an over simplification of the actual phenomenon. Even though the major contributions to the optical activity arises from the interaction of oscillators along the optic axis, the contribution from the interaction of all the other oscillators in the

system cannot be neglected. Further, the optical activity is found to increase linearly with temperature in the range from 15°C to 35°C in the visible region of the spectrum, and this is primarily due to a volume effect rather than a pure temperature effect.

Electroreflectance Studies By carrying out electroreflectance studies at oblique incidence on Ge and GaAs, it is shown that this technique is a particularly powerful method of observing the field-induced changes in the optical constants, which in turn facilitates the understanding of the band structure. Three features are added to the information available from measurements at normal incidence: namely (i) increased sensitivity near the Brewster angle, (ii) the electric field is applied both parallel and transverse to the direction of propagation of light, and (iii) capability of obtaining experimental data which described independently $\Delta\epsilon_1$ and $\Delta\epsilon_2$ thus eliminating the need for Kramers-Kronig dispersion analysis.

THESES DEGREES GRANTED

D. Felenzer, M.S. in Physics, 1968 "Electroreflectance at Oblique Incidence"

PAPERS PRESENTED

T. A. Davis and K. Vedam "Variation of the Refractive Indices of CaWO_4 and CaMoO_4 with Hydrostatic Pressure to 7 kbars", American Physics Society Meeting, Boston, February 1968

PUBLICATIONS

T. A. Davis and K. Vedam "Variation of the Refractive Indices of CaWO_4 and CaMoO_4 with Hydrostatic Pressure to 7 kbars", Bull. Amer. Phys. Soc. 11 13, 184 (1968)

K. Vedam and T. A. Davis, "Nonlinear Variation of the Refractive Indices of α -Quartz with Pressure" J. Opt. Soc. Amer. 57, 1140 (1967)

- M. B. Myers and K. Vedam, "Effect of Pressure on the Optical Rotatory Power and Dispersion of Crystalline Sodium Chlorate", J. Opt. Soc Amer 57, 1146 (1967)
- T. A. Davis and K. Vedam, "Photoelastic Properties of Sapphire (α -Al₂O₃)", J. Appl. Phys. 38, 4555 (1967).
- K. Vedam and T. A. Davis, "Piezo- and Thermo-Optic Behavior of LiNbO₃", Appl. Phys Let 12, 138 (1968).
- T. A. Davis and K. Vedam, "Variation of the Refractive Indices of Calcite, with Pressure to 7 kbars", Phys. Stat. Solidi 26, 285 (1968)
- E. D. D. Schmidt, J. L. Kirk and K. Vedam, "Variation of the Refractive Index of Diamond with Hydrostatic Pressure to 7 kbars". Amer Min (1968) (accepted for publication).

3.3.5

PROPERTIES OF CARBON

PERSONNEL

P L Walker, Jr , Professor of Materials Science
 D F Kline, Professor of Materials Science
 W S Diethorn Professor of Nuclear Engineering
 F J Vastola Associate Professor of Fuel Science
 R Phillips Research Associate, Fuel Science
 R Sappok, Research Associate Fuel Science
 D Brown, Research Assistant Fuel Science
 D J Allardice, Research Assistant, Fuel Science
 G Renshaw, Research Assistant, Fuel Science
 R P Gupta, Graduate Student, Solid State Science
 Y Ishikawa Graduate Student, Solid State Science
 G Michael, Graduate Student Solid State Science
 J J Santiago-Aviles, Graduate Student, Solid State Science
 P Blankenhorn, Graduate Assistant, Nuclear Engineering
 K O Lindquist, Graduate Assistant, Nuclear Engineering
 A Marshall, Graduate Assistant Nuclear Engineering
 W Woolson, NDEA Fellowship
 R Taylor, North American Fellowship

OTHER SPONSORSHIP

Atomic Energy Commission (AT(30-1)-1710)

RESEARCH REPORT

Studies in progress are (i) carbon monoxide disproportionation over well-defined metal crystals, (ii) electronic transport properties of boron-doped graphite at high measurement temperature and different atmospheres, (iii) kinetics and mechanism of C^{13} transfer to graphite C^{12} surface from $C^{13}O$; (iv) kinetics of metal oxide reduction by graphites of different active surface area; (v) kinetics of the gasification of graphite by oxygen, as influenced by traces of water vapor; (vi) electron spin resonance studies of carbon as affected by gas interaction (vii) Electron microscopy studies on fission recoil damage in single crystal graphite; (viii) studies relating defect concentration and type in single crystal

graphite to kinetics of fission Xe^{133} release rates; (ix) fast neutron damage (doses of 10^{22} nvt) in single crystal graphite using cleavage and decoration techniques; (x) effects of low temperature irradiations on the dynamic mechanical behavior of graphites; (xi) low temperature expansion effects in graphites and carbons.

THESES, DEGREES GRANTED

- J. M. Cardito, M.S. in Nuclear Engineering, 1967: "Capture of Ar^{41} by a Graphite Powder During the $\text{Ar}^{40}(\text{n}, \gamma)\text{Ar}^{41}$ Reaction".
- A. C. Marshall, M.S. in Nuclear Engineering, 1967: "The Effect of Radiation Damage and Thermal Annealing on the Release of Xe^{135} from Natural Graphite".
- R. E. Taylor, Ph.D. in Solid State Science, 1967: "Dynamic Mechanical Behavior of Graphites and Carbons".

PAPERS PRESENTED

None

PUBLICATIONS

- H. B. Palmer and M. Shelef, "Vaporization of Carbon", Chemistry and Physics of Carbon, Vol 4, Marcel Dekker, Inc. (1968).
- H. Cochrane, P. L. Walker, Jr., W. S. Diethorn and H. C. Friedman, "Xenon Adsorption on Graphitized Carbon Blacks over a wide Coverage Range", J. Colloid Interface Science 24, 405 (1967).
- R. O. Lussow, F. J. Vastola and P. L. Walker Jr., "Kinetics of Oxygen Interaction with Graphon Between 450-675°C", Carbon 5, 591 (1967).
- P. L. Walker, Jr., M. Shelef and R. A. Anderson, "Catalysis of Carbon Gasification", Chemistry and Physics of Carbon, Vol 4, Marcel Dekker Inc. (1968).

- R. E. Taylor, D. E. Kline and P. L. Walker, Jr., "The Dynamic Mechanical Behavior of Graphites", Carbon 6 (1968) (in press).
- P. J. Hart, F. J. Vastola and P. L. Walker, Jr., "Oxygen Chemisorption on Well Cleaned Carbon Surfaces", Carbon 5, 363 (1967).
- P. L. Walker, Jr., F. J. Vastola and F. J. Hart, "Oxygen - 18 Tracer Studies on the Carbon-Oxygen Reaction", Fundamentals of Gas-Surface Interactions, pp. 307-317, Academic Press, New York, New York (1967)

3.3.6 PROPERTIES OF GEL-GROWN LEAD IODIDE

PERSONNEL

H. K. Henisch, Professor of Applied Physics
A. Dugan, Graduate Assistant, Physics

OTHER SPONSORSHIP

None

RESEARCH REPORT

In this work, an attempt was made for one particular substance to relate defect structure and growth parameters, with some degree of success. At the same time, the opportunity was taken for optical and electrical measurements on crystals of a quality not hitherto available. As a result, the band and defect level structure of PbI_2 has been considerably clarified, and a number of anomalies noted in the literature have been explained. The detailed results are incorporated in a Ph. D. thesis and in the three published papers listed below.

THESES, DEGREES GRANTED

A. Dugan, Ph. D. in Physics, 1968: "Optical, Dielectric, Photoconductive and Photoluminescent Properties of Gel-Grown Lead Iodide Single Crystals".

PAPERS PRESENTED

A. E. Dugan, "Characterization of the Optical Photoconductive and Dielectric Properties of PbI_2 ", Honeywell Corporate Research Center, Hopkins, Minnesota, April 1967.

PUBLICATIONS

- A. Dugan and H. K. Henisch, "Dielectric Properties and Index of Refraction of Lead Iodide Single Crystals", J. Phys. Chem. Solids 28, 971 (1967).
- A. Dugan and H. K. Henisch, "Fundamental Optical Absorption and Photoconduction in PbI_2 Single Crystals", J. Phys. Chem. Solids 28, 1885 (1967).
- A. Dugan and H. K. Henisch, "Defect Energy Level Structure of PbI_2 Single Crystals", Phys. Rev. (1968) (in print).

3.4

RESEARCH ON GLASS

Under this heading we bring together several areas of work which form part of a "coupled" program, with the Naval Research Laboratory and Bausch and Lomb, Inc., dealing with glass as a solid state host. This major area of the program is being expanded, although due to the absence of any new funds so far, such expansion can only be achieved upon the orderly termination of research in other areas.

3.4.1

PREPARATION OF GLASSES

PERSONNEL

D. M. Roy, Senior Research Associate in Geochemistry
R. Roy, Professor of Geochemistry
P. T. Sarjeant, Graduate Student, Solid State Science
D. W. Strickler, Graduate Student, Solid State Science
S. P. Faile, Graduate Student, Solid State Science

OTHER SPONSORSHIP

Xerox Corporation
Atomic Energy Corporation (AT(30-1)-2581)

RESEARCH REPORT

Theory of Glass Formation and the use of Splat Techniques to Yield New Glasses. Most theories which purport to define the limits within which glass may be formed select as the most important parameters the structure or bonding of the liquid or solid. Yet the metastability of all glasses points clearly to a crucial role for the rate of quenching. In this study we have developed a wholly new treatment in which we are able to relate the rate of quenching to the ability to form glasses (N_g) with only one measurable "structural" parameter in the equation--the viscosity of the liquid (η). The only other adjustable parameter is " α_2 " the radius of the differing species.

The second part of the study consisted of attempts to apply the new splat quenching techniques to oxide melts to yield new glasses. Here we were very successful and obtained literally dozens of materials in glassy form which had previously been thought of as "unquenchable" (e. g. WO_3 , YAG, Mg_2SiO_4 , $KNbO_3$, etc.). Furthermore, the data were consistent with the theory outlined above within an order of magnitude (in the rate of quenching). Thus while $BaTiO_3$ should be glassy if quenched faster than $10^{50}C/sec$ and is, $MgAl_2O_4$ should be glassy even at

$10^{70}\text{C}/\text{sec}$ and this is also true. The alkali halides are quenchable only at $10^{90}\text{C}/\text{sec}$

New Photo-Conducting Glasses. The objective of this work has been to understand the conduction mechanism in an oxide glass and then to try to establish possible compositions which might stem photo-conduction. Our approach was based on a Goodenough model in which we hoped to generate narrow d-band formation by orbital overlap. This required a very high concentration of cations and this study concentrated on such glasses. We were, in fact, able to tailor make a whole family of transparent photo-conducting glasses with $\mu\tau$ products not very different from selenium. The highest photoresponse compositions were 65 mol % CdO, 15% B_2O_3 , 20% XO_2 where X was Si or Ge. Three important general findings emerged from an analysis of the chemical and structural data obtained by several methods. (i) very substantial electronic conduction bands (and photostimulation thereof) can be achieved even at room temperature in simple oxide glasses with variable valence oxides; (ii) impurities even at the 10 ppm level of metals such as Fe, Co, can completely mask the photo effects; (iii) the glass is definitely metastably unmixed to "two glasses" at such sub-micron level, and cannot be treated as a homogeneous phase.

The spectral response of the silicate peaks sharply just outside the visible. This is the present chief limitation on the utility of such materials.

High Concentrations of Gases in Glasses. Glasses containing up to several mole percent of gases including He, Ne, Ar, H_2 , O_2 , NH_3 , and CO_2 have been prepared at elevated temperatures and pressures. Solubility of the gases in the various glass-structures, stability of the glasses and conditions for phase separations have been determined. These solubilities can be used to test various models for families of glasses, such as the alkali borates.

Hydrogen-containing glasses have been found to be resistant to certain effects of radiation damage especially the formation of color centers in the visible and UV regions. Some of this research has major promise for application in protecting cover slips of solar cells and has also resulted in a patent application.

THESES, DEGREES GRANTED

- P. T. Sarjeant, Ph. D. in Solid State Science, 1967: "New Experimental and Theoretical Approaches to the Glassy State".
- D. W. Strickler, Ph D in Solid State Science, 1968: "The Preparation and Properties of Photoconducting Oxide Glasses."

PAPERS PRESENTED

- V. B. Caslavskaja, D W Strickler and R Roy, "Optimization of Properties of Photoconductive Glasses", American Ceramic Society Meeting, Chicago, April 1968.
- D. W. Strickler and R Roy, "New Transparent Photoconducting", Second International Conference on the Characterization of Materials, Rochester, New York, November 1967.
- P. T. Sarjeant and R Roy, "Parameters Controlling Formation of Short-Range-Order-Only Phases", Second International Conference on the Characterization of Materials, Rochester, New York, November 1967
- Della M. Roy and S P. Faile, "High Pressure Gas-Glass Systems: Destruction of Irradiation-Produced Color Centers", American Ceramic Society Meeting, Chicago, April 1968.

PUBLICATIONS

- D. M. Roy and S P. Faile, "Irradiation Effects of Glasses. Suppression by Synthesis Under High Pressure Hydrogen", *Science* 256, 1593 (1967).
- P. T. Sarjeant and R. Roy, "Splat Quenched Melts in the MgO-Al₂O₃ System", *J. Appl. Phys.* 38, 4540 (1967).
- P. T. Sarjeant and R. Roy, "A New Approach to the Prediction of Glass Formation", *Mat. Res. Bull.* 3, 265 (1968).
- P. T Sarjeant and R. Roy, "New Glassy and Polymorphic Oxides Using Rapid Quenching Techniques". *J Am. Ceram. Soc.* 50, 500 (1967).

V. B. Caslavskaja, D. W. Strickler and R. Roy, "Optimization of Properties of Photoconductive Glasses", Bull. Am. Cer. Soc. 47, 401 (1968).

3.4.2

STRUCTURE OF GLASSES

PERSONNEL

W. B. White, Associate Professor of Geochemistry
E. W. White, Assistant Professor of Solid State Science
B. E. Knox, Assistant Professor of Solid State Science
J. R. Sweet, Research Associate, Solid State Science
S. Varney, Graduate Student, Solid State Science
J. Berkes, Graduate Student, Solid State Science
J. Malone, Graduate Student, Geochemistry

OTHER SPONSORSHIP

National Science Foundation (GP-5102)

RESEARCH REPORT

Instrumentation for IR Spectra of Molten Glasses. A modification of an infrared spectrometer has been made which permits the measurement of vibrational spectra of glasses and liquids at high temperatures. Spectra are measured by specular reflectance from the liquid surface. A computer program transforms the specular reflectance spectrum to an absorption spectrum by means of a Kramers-Kronig analysis. The operating range is 2-15 microns at temperatures to 1000°C.

IR Spectra of Sodium Silicate Liquids. Spectra in the Si-O stretching region have been measured by specular reflectance techniques and absorption spectra calculated. These have been compared with specular reflectance spectra of polished glass and with KBr pellets of the same compositions. The spectra vary considerably with composition but only slightly with temperature.

Use of X-Ray Emission to Study the Borate Anomaly. Recently Bray has established by NMR techniques that the principal structural change at the so-called "borate anomaly" probably does not concern the B^{3+} coordination but may involve the Na^+ . This study is an attempt to examine the X-ray emission spectra of Na^+ and O^{2-} in a series of glasses which go across the borate anomaly

compositions. Preliminary results suggest that the X-ray changes may be too small to be of any use.

Laser-Mass-Spectrometry Studies of Glass-Structures. The reasoning behind these experiments is that if the pulsed burst of energy is large enough it will disrupt a structure into the smallest tightly bound units. By controlling the energy one can arrest this disintegration process between the atomic level and the species formed by equilibrium evaporation. If certain molecular fragments appear under a variety of conditions it is not unreasonable to assert that such units (or larger ones formed from them) do occur in the original glass. More details have been given in section 3.2.6.

Use of Crystal Field Spectra of Ni^{2+} to Study Structures of Borate Glasses In an attempt to understand the bonding of Ni^{2+} in a series of alkali borates, it has been dissolved in an analogous series of alkali- B_2O_3 glasses from Rb to Li. The crystal field splitting parameter has been shown to be very low (compared to Ni^{2+} in crystalline oxides such as MgO where it is near 800-850 cm^{-1}) and varies from 650 cm^{-1} for Li to 520 for Rb, illustrating the weakness of the bond between the Ni^{2+} and the borate network and possibly accounting for the success of such glasses as crystal growing fluxes.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

None

PUBLICATIONS

None

3.4.3

PROPERTIES OF GLASSES

PERSONNEL

V. Vand, Professor of Crystallography (deceased)
 W. B. White, Associate Professor of Geochemistry
 M. W. Balluffi, Research Associate, Solid State Science
 L. E. Cross, Professor of Electrical Engineering
 L. N. Mulay, Professor of Solid State Science

OTHER SPONSORSHIP

National Science Foundation (GP 5489)
 Atomic Energy Commission (AT(30-1)-2581)

RESEARCH REPORT

Dielectric Properties of Glass. A detailed study of dielectric and mechanical loss in the glass composition $1.5\text{Na}_2\text{O}:0.5\text{Al}_2\text{O}_3:5\text{SiO}_2$ is nearing completion. Data have been taken over some 5 orders in frequency, using Förster's method, a torsional pendulum, the rotating field and conventional dielectric bridge methods. Arrhenius type plots show an activation energy $E_a = 0.725 \pm .03$ eV identical within experimental error for both dielectric and mechanical processes, but a constant separation between the two curves such that $\tau_{\text{dielectric}} = 1.5 \tau_{\text{elastic}}$.

It is clear that the dielectric loss in this system is from a short range migration of the Na^+ ions and not of a Maxwell-Wagner type. It is probable that the factor 1.5 is a reflection of the lengthening of the macroscopic τ in the dielectric case due to internal field effects.

Magnetic Properties of Glass. This work is an attempt to use the observed supereparamagnetism of certain glasses to describe the process of preparation of a second phase from glasses. It has already been described in Section 3.3.2.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

None

PUBLICATIONS

None

3.5 SOLID STATE BIOSCIENCE AND GEOSCIENCE

In this section we bring together all the work in which the principles of solid state chemistry and physics are applied to biologically or geologically oriented problems. Due to the lack of laboratory space, our expansion into these fields had to be suspended two years ago. However, as we move into the new building the faculty's plans are to make Solid State Bioscience a major emphasis in our work.

3.5.1 TRACE METAL AND MAGNETIC PROPERTIES OF ANIMAL MATERIALS

PERSONNEL

(Mrs.) I. L. Mulay, Research Associate, Bioscience
L. N. Mulay, Professor of Solid State Science
R. Roy, Professor of Geochemistry
B. E. Knox, Assistant Professor of Solid State Science
N. H. Suhr, Assistant Director of the Mineral Constitution
Laboratory
B. Des-Marais, Research Assistant
J. Hach, Research Assistant

OTHER SPONSORSHIP

Public Health Service (GM09487)
American Cancer Society (T-250)

RESEARCH REPORT

Trace Metal Analysis of Cancerous and Noncancerous Human Tissues. The purpose of this study was to determine various trace metals in cancerous and noncancerous human tissues and to see whether any significant differences existed in their concentration.

Of the metals found in man, some are known to be essential, others have no known function and a few are suspected to be carcinogenic agents.

In an exploratory survey, many tissues from healthy people and those suffering from various kinds of cancers were analyzed. It was apparent that even among healthy people there was a great variation of a specific trace metal content in a given organ, the variations attributable to age, sex, and diet. Therefore, normal and cancerous tissue were difficult to compare, although the range of "normal" values may be inferred from the data.

To overcome this problem, a new approach was devised. Samples of normal and cancer tissues, called "paired" samples, were obtained from the same individual. With this procedure, the variations between individuals were eliminated, and the results became meaningful.

The tissues were removed during surgery or autopsy at Jefferson Medical College Hospital in Philadelphia. A complete histopathological analysis was performed on each sample to ascertain whether it was normal or cancerous. If the sample was cancerous, the percentage of cancerous cells was also determined. Samples were prepared for trace metal analysis by freeze-drying and then ashing. The analyses were made by emission spectrography, a rapid, sensitive method for analyzing many elements. During procurement, preparation, and analysis of the samples, extreme care was taken to avoid contamination from the surroundings. The following twenty-two trace metals and two so-called bulk metals were also examined: aluminum, barium, beryllium, bismuth, cadmium, calcium, chromium, cobalt, copper, gallium, iron, lead, magnesium, manganese, molybdenum, nickel, silver, strontium, tin, titanium, vanadium, yttrium, zinc and zirconium. The following types of cancer were studied: cancer of the breast (two types: ductal carcinoma and scirrhous carcinoma), cancer of the lung (one type: squamous cell carcinoma), and cancer of the colon (one type: adenocarcinoma).

Results of the analyses were recorded as parts of metal per million parts of the tissue (dry weight), and the data were analyzed to find out whether the differences observed between cancerous and noncancerous tissues were statistically significant.

The results showed that in all types of cancer of the breast, copper, manganese, magnesium and zinc contents were much higher than in noncancerous breast tissue. No significant differences were found in amounts of other metals examined.

In cases of adenocarcinoma of the colon, the tin content was much lower in cancerous tissue than in noncancerous tissue. Amounts of other metals did not differ significantly.

Analysis of cancer of the lung showed that iron in cancerous lung was lower than in noncancerous lung; whereas zinc content was higher.

These results show that a significant difference in the concentration of selective metals is noticeable between cancerous and noncancerous tissues. At the same time, it is apparent that these differences pertain to a specific type of cancer. This specificity shows that all types of cancers cannot be lumped together but should be regarded as a separate entity for purposes of interpretation.

Magnetic and E. P. R. Studies on Free Radical Activity in Normal and Cancer Tissues. A study of magnetic susceptibility and electron paramagnetic resonance spectra of melanoma (melanotic and amelanotic) and normal tissues from mice showed significant differences in line shapes, and intensities. The intensities and values have been successfully correlated with trace metal analysis and known biochemical reactions. The free radical activity and the concentration of Cu^{2+} and Fe^{3+} was generally higher in the melanotic (S-91) tumor than in the amelanotic tumor. Other tissues such as liver, spleen, heart, kidney, brain, etc. showed varying amounts of free radical activity, but considerably less than in the cancerous tissues and did not reveal E. P. R. signals attributable to paramagnetic ions. These findings suggest that free radical activity in melanoma (S-91) may be attributed partly to melanin and intermediates of various enzymatic reactions. Similar biomedical information has been obtained in other cases.

THESES, DEGREES GRANTED

None

PAPERS PRESENTED

Indu L. Mulay, "Magnetic Susceptibility and E. P. R. Studies on Mouse Melanomas", Symposium on Bioscience, Madison, Wisconsin, June 1966.

PUBLICATIONS

Indu L. Mulay, "Magnetic Susceptibility and E. S. R. Absorption Spectra of S-91 and S-91 A Mouse Melanomas", J. Nat. Cancer Inst. 39, 735 (1967).

Indu L. Mulay, "Copper and Free Radical Accumulation in Liver of Calves with Inherited Hydrocephalus", Am. J. Vet. Res. 28, 1909 (1967).

Indu L. Mulay, "Magnetic Susceptibility: Recent Aspects of Instrumentation and Applications to Chemistry and Solid State Science", Analyt. Chem. 40, 440R (1968).

Indu L. Mulay, "Trace Metal Analysis of Cancerous and Non-cancerous Tissues" (in preparation).

3.5.2 PROPERTIES OF BIOGENIC AND OTHER COMPLEX NATURAL MATERIALS

PERSONNEL

J. Weber, Associate Professor of Geochemistry
P. J. Woodhead, Scientific Director, Heron Island Research
Station
R. T. Greer, Graduate Student, Solid State Science

OTHER SPONSORSHIP

National Science Foundation (GA-290)
Public Health Service (AM-10734)
NASA (Institutional grant to Pennsylvania State University)

RESEARCH REPORT

Mechanical Properties of Skeletal Materials. Unconfined compressive strength measurements have been made on single-crystal, high-magnesium calcite echinoid spines. The high strength to weight ratio of these skeletal elements is related to a regular fenestrate structure, the morphology of which has been studied by means of scanning electron microscopy.

Carbon and Oxygen Isotope Fractionation in Echinoderm and Coelenterate Carbonates. The mechanisms by which stable carbon and oxygen isotopes are fractionated in the precipitation of calcite by echinoderms and aragonite by coelenterates have been elucidated. Carbon-14 studies are in progress.

Fluorescence of Silicate Minerals. Variations of intensity and wavelength of optical fluorescence spectra obtained from silicates such as serpentines and pyroxenes have been correlated with variations in chemical composition. Fluorescence studies of natural silicates are oriented toward lunar applications.

THESES, DEGREES GRANTED

- R. T. Greer, Ph. D in Solid State Science, 1968: "Cathodoluminescence of Enstatite from Chondritic and Achondritic Meteorites and its Selenological Implications".

PAPERS PRESENTED

- J. Weber, "Dominance of Biological Effects on the Distribution of Stable Carbon and Oxygen Isotopes in the Skeletal Calcites of Echinoderms", invited paper, Fifth International Symposium Stable Isotopes, Leipzig, D. D. R., October 1967.
- J. Weber, "Geochemical Studies in Coral Reef Environments", invited paper, McMaster University, February 1968.
- R. T. Greer, "Developments in Luminescence Applications", invited paper, University of Pittsburgh, November 1967.
- R. T. Greer, "Developments in Quantitative Luminescence", Sixth Anniversary Meeting, Working Group on Extraterrestrial Resources, 1968.
- R. T. Greer, "Application of Luminescence Techniques to the Study of the Lunar Surface", Symposium Interpretation of Lunar Probe Data, Huntingdon Beach, California, January 1968.
- R. T. Greer, "Electron Excited Fluorescence of Enstatite Chondritic and Achondritic Meteorites", Anniversary Meeting, Geological Society of America, November 1967.

PUBLICATIONS

- J. N. Weber, "Possible Changes in the Isotopic Composition of the Oceanic and Atmospheric Carbon Reservoir with Geologic Time", *Geochim Cosmochim. Acta* 31, 2343 (1967).
- E. G. Williams, R. E. Bergenback and J. N. Weber, "Relationship Between Paleotopography and the Thickness and Geochemistry of a Pennsylvania Freshwater Limestone", *J. Sed. Petrol.* (1968) (in press)

- J. N. Weber, R. T. Greer and V. Vand, "Electron-Excited Fluorescence of Serpentine", *Planetary and Space Sci.* 15, 633 (1967).
- J. N. Weber and D. M. Raup, "Comparison of C^{13}/C^{12} and O^{18}/O^{16} in the Skeletal Calcite of Recent and Fossil Echinoids", *J. Paleo.* 42, 37 (1968).
- J. N. Weber and P. Deines, "Erroneous Conversion of Carbon Isotope Data--Comments on a Paper by Cheney and Jensen", *Geochim. Cosmochim. Acta* 31, 1343 (1967).
- J. N. Weber, "Factors Controlling the Carbon and Oxygen Isotopic Composition of Marine Carbonate Sediments, Part I. Bermuda", *Amer. J. Sci.* 265, 586 (1967).
- J. N. Weber, "Fractionation of the Stable Isotopes of Carbon and Oxygen by Calcareous Marine Invertebrates--the Asteroidea, Ophiuroidea, and Crinoidea", *Geochim. Cosmochim. Acta* 32, 33 (1968).
- J. N. Weber, "Dominance of Biological Effects on the Distribution of Stable Carbon and Oxygen Isotopes in the Skeletal Calcites of Echinoderms", *Studia Biophysica* 4, 191 (1967).
- J. N. Weber, "Quantitative Mineralogical Analysis of Carbonate Sediments--Comparison of X-Ray Diffraction and Electron Probe Microanalyzer Methods", *J. Sed. Petrol.* 38, 232 (1968).
- J. N. Weber and R. F. Schmalz, "Factors Controlling the Carbon and Oxygen Isotopic Composition of Marine Carbonate Sediments, Part III Eniwetok Atoll", *J. Sed. Petrol.* (1968) (in press).
- J. N. Weber and P. Woodhead, "Factors Controlling the Carbon and Oxygen Isotopic Composition of Marine Carbonate Sediments, Part II. Heron Island, Great Barrier Reef, Australia", (1968) (submitted for publication).
- J. N. Weber, R. T. Greer, B. Voight, E. White and Rustum Roy, "Strength of Echinoderm Calcite Related to Structure", (1968) (submitted for publication).

- J. N. Weber, "Stable Isotope Mass Spectrometry", to appear as a chapter in Modern Methods of Geochemical Analysis, ed. by R. E. Wainerdi (1968).
- J. N. Weber, "Incorporation of Magnesium into the Skeletal Calcites of Echinoderms", (1968) (submitted for publication).
- R. T. Greer and V. Vand, "Electron Excited Fluorescence of Enstatite Chondritic and Achondritic Meteorites", Spec. Paper Geol. Soc. Amer. (1968) (in press).
- R. T. Greer, V. Vand and J. N. Weber, "Applications of Luminescence Techniques to the Study of the Lunar Surface. Interpretation of Lunar Probe Data, Part II.", Amer. Astron. Soc. (1968) (in press).
- R. T. Greer, V. Vand, J. N. Weber and E. W. White, "Developments in Quantitative Luminescence", Proc. 6th Ann. Meet., W. G. E. R. (1968) (in press).
- W. A. Schlosser, R. T. Greer and V. Vand, "Computation and Interpretation of Insolation Tables for the Surface of Mars", Trans. Amer. Geophys. Union 49, 250 (1968).

3.5.3 STRUCTURE AND PROPERTIES OF WATER

PERSONNEL

V. Vand, Professor of Crystallography (deceased)
M. W. Barnes, Research Associate, Solid State Science

OTHER SPONSORSHIP

None

RESEARCH REPORT

A model of liquid water is formed by assigning, in a random fashion, hydrogen bonds to lattice sites. The fraction of each configuration is then counted, providing a concentration of each configuration "species". The simplest model, that of a two-dimensional square lattice, has been calculated. The concentrations obtained are in reasonable agreement with those from infrared spectral experiments. Currently being studied is the effect of cooperativity: a bond which closes a ring is expected to form most easily. Extending the calculations to include the third dimension and dissolved ions is planned.

THESES, DEGREES PRESENTED

None

PAPERS PRESENTED

None

PUBLICATIONS

None

4.0 SCIENCE AND TECHNOLOGY TRANSFER

The laboratory has had for several years substantial effort in this field of interpretation of materials science, continuing education to industrial personnel and interaction with industrial and government personnel. These were greatly expanded last year with State Technical Service Company support.

4.1 MATERIALS ADVISORY PANEL PROGRAM

PERSONNEL

Rustum Roy, Director
Ernest M. Hawk, Coordinator

OTHER SPONSORSHIP

PENNTAP - Pennsylvania Technical Assistance Program, funded by the federal and state Departments of Commerce

MAP-GSAC - Materials Advisory Panel of the Governor's Science Advisory Committee (Pennsylvania)

REPORT

The MAP Training Program is designed to equip Pennsylvania industrial scientists and engineers with the latest research data and information in materials science and technology. The program utilizes several information transfer devices: (i) identical travelling one-day seminars, held in strategic locations around the state; (ii) two-day workshops concentrating on laboratory demonstrations of problem-solving techniques, and (iii) short courses programmed in such a way (evening sessions, one day a month, etc.) as to fit into the work schedule of the industrial attendee.

Technical content and supervision of the program is provided by a consortium of the Commonwealth's outstanding university and industrial research leaders in the materials field. The Pennsylvania State University, through its Continuing Education Services, handles the business and promotional aspects of the program.

Below are listed the actual programs carried out under this program, jointly by all the major universities of the state and its major materials industries.

One-Day Travelling Seminars (3 series of 3 days each)

Composite Materials

Joining of Metals

Biomaterials: Materials in Medicine and Dentistry

Two-Day Workshops (3)

Problem-Solving in Modern Materials Engineering

Short Course

Metalworking Under High Pressure

4.2 INDUSTRIAL COUPLING PROGRAM

PERSONNEL

Rustum Roy, Director
Ernest M. Hawk, Coordinator

OTHER SPONSORSHIP

Ten industrial firms and the Materials Research Laboratory

REPORT

The Materials Research Laboratory is firmly committed to an effort to "couple" more quickly and effectively the basic science being conducted at the University to the applied science of the country's industrial research laboratories. Thus it established the Industrial Coupling Program in 1964. Building on established relationships with a small group of companies, this program fosters a more intensive transfer of information in research areas of mutual industry-university interest. This is accomplished through an annual meeting of all concerned industrial and university personnel and periodic mailings of research reports, theses, and notices of relevant seminars and lectures.

Industrial organizations benefit by having close contact with a large research group working in various specialized areas of the materials field, from the advantages of an interdisciplinary approach to complex research and development problems, and by having a head-start opportunity for recruitment of promising students nearing graduation.

The Materials Research Laboratory is strengthened by continuing relationships with specific industries which inform and sharpen its research activities, and by financial support which provides fellowships for promising graduate students, special opportunities to bring visiting national and international scientists to the campus, and purchase of needed equipment and library reference material.

4.3 PENNSYLVANIA TECHNICAL ASSISTANCE PROGRAM TELEVISION PROJECT

PERSONNEL

Heinz K. Henisch, Program Director
Clifford A. Hewitt, Program Coordinator

OTHER SPONSORSHIP

Pennsylvania Technical Assistance Program

REPORT

Under provisions of the State Technical Service Act, the Pennsylvania Technical Assistance Program offers various services to business and industry in the state of Pennsylvania. The Materials Research Laboratory was awarded a contract by PennTap to produce a series of six television programs on materials science in partial fulfillment of this purpose.

Six TV programs were produced under the general title "Looking at Materials". Kinescope 16mm. film copies are available of each program. Subtitles of individual programs are: (i) Crystal Growth; (ii) Composites; (iii) Characterization; (iv) Crystal Growth in Gels; (v) Modern Ceramics; and (vi) High Pressure.

4.4 A CARBON INFORMATION RETRIEVAL SYSTEM

PERSONNEL

D. L. Walker, Jr., Professor and Head, Materials Science
G. Johnson, Jr., Assistant Professor of Computer Science
S. Marin, Literature Searcher
E. Hepner, Keypuncher
E. Gardner, Graduate Assistant, Computer Science

OTHER SPONSORSHIP

Pennsylvania Technical Assistance Program

REPORT

The purpose of building a data file containing information on carbon and graphite products is for distribution of information within the state of Pennsylvania. The project was initially funded on April 1, 1968. Since that time approximately 3000 source references have been abstracted and keypunched for title, author, location of author, journal reference, language, and keywords. The information is being entered into a computer retrieval system being written specifically for this project. The present state of the project concerns the checking of the programs on a small (100 entries) section of the file to ascertain that the logic of the programs is correct.

Lists of contents of the file and the methods of retrieval first will be distributed to interested Pennsylvania industries in the third quarter of 1968. The system will be run by the above personnel for the next two years while possible methods of improved retrieval are developed.

4.5 X-RAY EMISSION WAVELENGTH TABLES PRODUCTION

PERSONNEL

E. W. White, Assistant Professor of Solid State Science
G. G. Johnson, Jr., Assistant Professor of Computer Science
L. B. Taylor, Graduate Assistant, Computer Science
R. McMillan, Graduate Assistant, Computer Science

OTHER SPONSORSHIP

American Society for Testing and Materials

REPORT

The standardization of X-ray wavelengths has been the recent work of Dr. J. A. Bearden of Johns Hopkins, who has communicated the data to the personnel of this report. With the additional reliability of his data and the measurement of the long wavelength region by Dr. A. Burr, the forthcoming revised publication, "X-Ray Wavelengths and Two Theta Tables [E. W. White, G. G. Johnson, Jr., et al., ASTM DS-37 (1965)] will prove to be much more useful than previous compilations. The investigation here at the Pennsylvania State University during the last year includes satellite lines, relative intensities, absorption edges, correction for index of refraction and more refracting crystals for the purpose of improving the data in the book. The new compilation with all of the above improvements will be produced about January 1, 1969. The publication will be distributed by ASTM as a continuing reference of the fundamental constants of X-ray spectra.